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THE CATALYTIC OXIDATION OF ETHYLENE TO ETHYLENE OXIDE[1]

BY F. L. W. MCKIM AND A. CAMBRON

Abstract

The catalytic oxidation of ethylene to ethylene oxide was investigated in flow experiments over silver catalysts at atmospheric pressure between 260° and 350° C. Calcium oxalate and stannous oxide were used as catalyst promoters. Close temperature control was provided by mounting the catalyst on a silver support. At 270° C. the selectivity increased from about 25%, with ethylene in large excess, to about 55%, with oxygen in large excess. With air constant and in large excess, the over-all reaction rate was found to be proportional to the square root of the ethylene concentration. With ethylene constant and in large excess, the reaction rate was found to be roughly proportional to the oxygen concentration. The presence of methane, ethane, or propane promoted the complete oxidation of ethylene to carbon dioxide and water. In the absence of paraffins the addition of traces of ethylene dichloride only served to poison the catalyst.

Introduction

Ethylene oxide was first prepared by Wurtz (38) in 1859 by the action of alkali on ethylene chlorhydrin. The latter compound, which Wurtz had also been the first to prepare, had been obtained by the action of hydrochloric acid on ethylene glycol. The method used by Wurtz for preparing the oxide is still the most convenient laboratory method and is also one of the commercial methods in use to-day for preparing that chemical, which is becoming increasingly important as a starting material in organic syntheses.

During the past 20 years another and more direct method for obtaining ethylene oxide has been investigated. This method consists in the oxidation of ethylene by elementary oxygen to ethylene oxide. In an investigation of the noncatalytic reaction between ethylene and oxygen, Lenher (21) found ethylene oxide and formaldehyde to be the primary reaction products. Other oxidation products identified by Lenher were dioxymethyl peroxide, acetaldehyde, formic acid, water, and the oxides of carbon. Lenher found that both the rate of reaction and the amounts of the various reaction products were influenced by the nature and extent of the surface of the reaction vessel. He concluded that some steps of the reaction took place at the wall of the vessel. This method for the preparation of ethylene oxide was the subject of a patent assigned to duPont (22). Geib and Harteck (11) reported the formation of ethylene oxide when oxygen atoms reacted with ethylene at −183° C.

[1] *Manuscript received July 13, 1949.*

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Recently, Newitt and Mene (27) have reported obtaining ethylene glycol by the oxidation of ethylene at pressures between 10 and 100 atm. at 200° C.

Subsequent to Lenher's publication, Francon (10) published the results of an investigation of the catalytic oxidation of ethylene to ethylene oxide. Ethylene oxide, carbon dioxide, and water, together with traces of aldehydes, were the only oxidation products. In this paper Francon described the conditions under which the reaction was carried out but did not disclose the preparation or composition of the catalyst. Francon's method was the subject of several patents assigned to Société Française de Catalyse Généralisée (33) and to Carbide and Carbon Chemicals Corporation (20). Although the first reference to the use of silver as a catalyst in the air oxidation of ethylene was made by Walter (37), the former patents (20, 33), and those assigned to Dreyfus (9) were the first disclosures of the use of silver as a catalyst in the vapor phase oxidation of ethylene to ethylene oxide. Several other metals, such as antimony, lead, copper, and iron, were also claimed to be active as catalysts in this reaction; but in the course of later investigations silver was found to be the only practical catalyst and in the numerous later patents the use of silver has been the subject of specific claims.

Reference to the use of silver as a catalyst for the oxidation of ethylene to ethylene oxide has also appeared in a thesis by A. Hecker (12) and in a paper by Reyerson and Oppenheimer (31), who described experiments in which they compared the activity of silver catalysts prepared by different methods with the activity of a silver catalyst claimed to be in commercial use for the production of ethylene oxide. McBee, Hass, and Wiseman (24) have reported an investigation of the catalytic air oxidation of ethylene using a silver catalyst prepared by coating pieces of corundum with silver oxide.

More recently Twigg (34) has investigated the mechanism of the silver catalyzed oxidation of ethylene by experiments in both flow and static systems. He concluded that the first step in the reaction is adsorption by the catalyst of oxygen in the form of atoms. Ethylene, which was found to be either not adsorbed at all or only weakly adsorbed by Van der Waal's forces, would then react either with one adsorbed oxygen atom to form ethylene oxide or with a pair of atoms to form an intermediate that is rapidly oxidized to carbon dioxide and water. Some of the carbon dioxide and water may also be formed by oxidation of the ethylene oxide via acetaldehyde.

The aim of the present work was the production of an active and stable silver catalyst and the development of a reactor design that would give close temperature control of the catalyst surface. The effect of the presence of methane and ethane on the reaction were also to be investigated.

Choice of Catalyst Support

The formation of ethylene oxide from ethylene and oxygen is a mildly exothermic reaction:

$$C_2H_4 + 1/2O_2 \longrightarrow C_2H_4O + 29.2 \text{ kcal. } (280° \text{ C.})$$

but the complete combustion of ethylene to carbon dioxide and water is strongly exothermic:

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + 317 \text{ kcal. } (280° \text{ C.})$$

It was realized that one of the major problems in controlling reaction conditions was the design of a reactor that would provide a large catalyst area per unit volume but would allow close temperature control at all points of the catalyst surface.

Although Langwell *et al.* (17) have recommended coating the catalyst in a thin layer on a removable metal support in a tube bundle heated by a boiling liquid, all the other workers in this field have used as the catalyst support refractory materials such as fused alumina pellets (5), sandstone, porous artificial silica filter stone (18) and fire brick (26). When glass wool or fused alumina pellets were used as supports for an active silver catalyst in preliminary experiments in Pyrex tubes, it was observed that as the ethylene rate was increased, the entrance end of the catalyst bed would begin to glow, the local rise in temperature resulting in excessive carbon dioxide formation and in sintering and deactivation of the catalyst.

This defect of catalyst supports of low thermal conductivity has been reported by several workers. Hecker (12), using a silver catalyst supported on glass wool, reported a decrease in selectivity* from 48 to 30% as the ethylene concentration was increased from 3 to 13%. McBee *et al.* (24) showed that good temperature control could be obtained with a corundum catalyst support at low ethylene rates. In one series of experiments, however, they reported a decrease in the ethylene oxide produced as the total flow rate was increased. This was very probably caused by increased combustion of the ethylene to carbon dioxide and water resulting from poor temperature control at the higher flow rate.

The laboratory reaction tubes described below, in which silver sheet is used as the catalyst support, were used in an attempt to solve the temperature control problem in laboratory experiments. A description of the "fin reactor", which was felt to be easily adaptable to larger scale experiments, will form the subject of a later communication.

Methods of Preparation of Silver Catalysts

The methods disclosed in the literature for preparing finely divided silver or silver oxide include the following, most of which have been patented as methods for preparing silver catalysts.

1. The thermal decomposition of silver salts of nitrophenols (13), silver oxalate (12, 15, 35), silver cyanide (28), silver carbonate and silver oxide (16).
2. The precipitation of silver oxide by the addition of a solution of sodium hydroxide to aqueous silver nitrate (32).

* *The term selectivity is used to denote the per cent yield of ethylene oxide based on ethylene reacted.*

3. The reduction of silver nitrate with hydrogen (6).
4. The reduction of silver compounds in an aqueous medium by nascent hydrogen (36).
5. The electrolysis of solutions of potassium nitrate or silver nitrate between silver electrodes (29).
6. The reduction of silver compounds by various reducing agents—e.g., formaldehyde, hydrazine, hydroxylamine (7).
7. Reduction of silver chloride with ferrous citrate (30).

Promoters

In addition to disclosing silver as a catalyst in the catalytic oxidation of ethylene to ethylene oxide, the original Lefort patent (20) disclosed gold, copper, iron, antimony, bismuth, lead, nickel, tin, arsenic, both as catalysts in their own right and as promoters with silver. Van Peski (35) reported gold, copper, and manganese as useful promoters, manganese also being used later by Hecker (12). Carter (5) disclosed that small amounts of compounds of alkali and alkaline earth metals, when used with silver supported on fused aluminum oxide, improved the activity and ruggedness of the catalyst. In a later patent, McNamee and Blair (25) reported that the oxides, hydroxides, and peroxides of barium, strontium, and lithium were the most useful oxides, hydroxides, and peroxides of the alkali and alkaline earth metals. Calcium oxides or hydroxide were also reported to increase the activity of the catalyst but the increased activity was accompanied by excessive carbon dioxide formation. Recently Mawer (26), in contradiction to McNamee and Blair, has reported calcium peroxide as an active promoter for silver in his reaction, and obtained selectivities as high as 64 to 68% without the use of an inhibitor.

Experimental

Preparation of Catalyst

In addition to the method described below, a number of methods of preparing an active silver catalyst were investigated, such as the thermal decomposition of silver oxalate in xylene at 200° C., in aqueous monoethanolamine at 60° C., the reduction of silver sulphite by monoethanolamine at 90° C., the precipitation of silver oxide by sodium hydroxide at 20° C., and the decomposition of silver nitrite at 300° C. The particle size of the silver catalysts prepared by the above methods was determined by the X-ray diffraction method and found to lie between 100 to 150 Å units.

It was found that the activity of unpromoted silver catalysts prepared by precipitation of silver or of silver oxide, or by thermal decomposition of an organic silver salt, was a function of the particle size of the silver, and was independent of the method used in their preparation.

The method used for the preparation of the catalyst in our experiments was the thermal decomposition of silver oxalate in the presence of water in an autoclave, sufficient water being added to maintain a liquid phase during the exothermic decomposition; this prevented local overheating and sintering of

the silver. Rapid decomposition of the oxalate began at about 110° C. and caused the temperature of the charge to rise to about 200° C.

Previous investigators who prepared finely divided silver by the thermal decomposition of the oxalate used dry silver oxalate as starting material (12, 15, 35). We found this procedure unsatisfactory on account of the explosive nature of the dry silver salt. By proceeding as outlined above, the decomposition of the oxalate takes place smoothly and a uniformly fine product is obtained with a particle size, as determined by the Laue–Brill method, of about 130 Å.

Pure silver catalysts prepared by any of the methods mentioned above showed a high initial activity when used at about 300° C., but the activity decreased rapidly owing to sintering. The stability and activity of such catalysts were found to be greatly increased by the addition of small percentages of calcium oxalate and stannous oxide. The calcium oxalate was coprecipitated with the silver oxalate, before decomposition, from a nitrate solution with sodium oxalate. The optimum amount of calcium oxalate has been found to be between 1 and 10% of the finished catalyst. Stannous oxide was added to the mixed silver–calcium oxalates either before or after thermal decomposition of the oxalates. The amount used was 2 to 10% of the silver.

Calcium oxalate and the oxides of tin and cadmium were investigated as promoters for silver because of the proximity of the oxide crystal lattice dimensions to those of silver oxide.

TABLE I

CRYSTAL LATTICE DIMENSIONS (ANGSTROM UNITS)

Substance	System, structure	Lattice constants		
		(a)	*(b)*	*(c)*
Ag	Cub., f.c., (Cu)	4.078	—	—
Ag_2O	Cub., f.c., (Cu_2O)	4.72	—	—
CaO	Cub., f.c., (NaCl)	4.797	—	—
SnO	tetr. (PbO)	3.77	—	4.77
SnO_2	tetr.	4.72	—	3.16
CdO	Cub., (NaCl)	4.689	—	—

Example

Two hundred grams of silver nitrate and 3.1 gm. of calcium nitrate ($Ca(NO_3)_2 \cdot H_2O$) were dissolved in 1.5 liters of distilled water. Eighty-four grams of sodium oxalate was dissolved in 1.5 liters of distilled water at 60° C.; this solution was filtered and added with stirring to the silver nitrate solution. The precipitate was allowed to settle, the supernatant solution decanted, and the precipitate stirred three times with 3 liters of distilled water, the precipitate being allowed to settle, and the clear liquid decanted between each washing. The precipitate was then filtered by suction and stored in a dark space.

The thermal decomposition of the mixed oxalates was effected by heating in the presence of water in an autoclave. One hundred and eighty grams of the mixed silver–calcium oxalates was made up into a paste with 160 cc. of water in a silver cylinder that fitted snugly in the autoclave. Before heating the autoclave, the air was swept out with carbon dioxide and after closing the autoclave the temperature was raised to 200° C. The observed pressure at this temperature was 175 kgm. per sq. cm. The heating cycle was approximately 15 min. heating to 200° C., 45 min. cooling to 150° C., at which temperature the pressure was released.

In order to obtain the catalyst in a form suitable for application to the metal support, the product obtained by the thermal decomposition of the silver and calcium oxalates was mixed with glycol in the proportion of 50 gm. of glycol to 100 gm. of catalyst. Finely ground stannous oxide (−325 mesh) was added at this point in the proportion of 2% of the weight of the silver. In order to break up the small aggregates of silver formed during the thermal decomposition of the oxalates, the glycol–catalyst mixture was milled for 15 hr. in a 1 liter Abbé mill with two steel cylinders 1 by 3½ in. By this treatment the catalyst was obtained as a thin paste that could be applied to a metal surface by brushing. The amount of dry catalyst required to coat a metal support in this manner was about 70 gm. per sq. m. A paste of suitable consistency for application to a metal support by dipping or spraying may be obtained by adjusting the proportion of glycol.

The silver nitrate, sodium oxalate, and calcium nitrate used were of "A.R." purity. The stannous oxide labeled "Pure" was obtained from the City Chemical Corporation, New York.

Apparatus and Experimental Procedure

Catalyst Supports and Reaction Tube

Fig. 1 shows the reaction tube, constant temperature bath, and two types of silver sheet catalyst supports used in our experiments.

The silver disk support, *A*, consisted of 15 disks, 1 by 1/32 in., coated with catalyst and spaced 1/10 in. apart by snugly fitting silver rings. Area of disks coated with catalyst, 135 sq. cm.; free space, 20 cc. This design, although providing a larger catalyst area per unit volume than the "star" support described below, had certain defects and was later discarded. Separation of the rings from the disks after repeated heating and cooling was observed with 2-in. disks in a 2 in. tube, and adequate temperature control was difficult with reactors larger than 1 in. diameter. This was due to the poor thermal contact between the disks and the tube wall. Difficulty was also frequently encountered in packing the disks and rings properly in the tube.

Another catalyst support used in laboratory experiments to evaluate catalysts was the "star" welded silver strip support, *B*, shown in Fig. 1. The "star" support used in the experiments reported below was 4½ in. long by 1 in. in diameter and consisted of ten 4⅜ by ⅜ by 1/32 in. silver strips welded

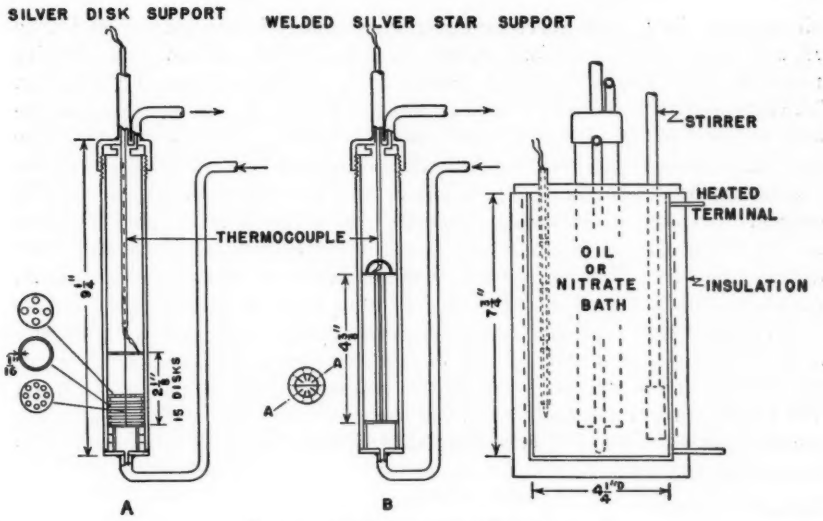

FIG. 1. *Stainless steel reaction tube.*

to silver rings at both ends. The area of the silver strips was 212 sq. cm. and the free space was 55 cc. One and one-half to two grams of a silver catalyst mixed in a smooth paste in glycol was required to coat this support by brushing. The use of a one-piece silver support has a definite advantage over a discontinuous support such as the one described above in that the true temperature of the catalyst can be more accurately measured by one thermocouple brazed to the support.

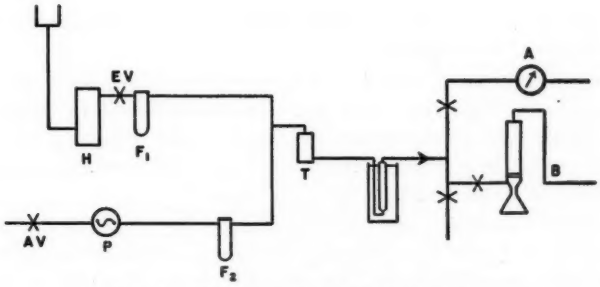

FIG. 2. *Diagrammatic sketch of apparatus.*

The assembled apparatus is shown diagrammatically in Fig. 2. The ethylene was stored in a 30 liter gas holder, *H*, under a constant 7 ft. head of water. The flow of ethylene was regulated through the valve, *EV*, and measured through the glass capillary flow meter, F_1. When other gases, such as methane, ethane, propane, hydrogen, or carbon dioxide were added to the

air–ethylene feed, these gases were stored separately in gas holders similar to *H*, and were metered through individual flow meters. During quantitative tests the ethylene was measured directly from a 1 liter calibrated gas holder. The air supply was measured through the flow meter, F_2. It was found advisable to insert in the air line a small tower containing cotton wool and active charcoal to remove any oil spray from the compressor and any other impurities such as hydrogen sulphide that might appear from time to time in the air supply. A tower of indicating "Drierite", *T*, inserted in the gas line after mixing of the air and ethylene was found useful in maintaining a uniformly dry gas mixture. The off-gas rate was measured by a wet test meter, *A*. An absorption tower, *B*, fitted with a 30 mm. sintered glass diaphragm was used in analyzing the off-gas for ethylene oxide and carbon dioxide. Chromel-alumel thermocouples and a Leeds & Northrup potentiometer were used to measure the temperatures of the catalyst support and of the oil bath (Fig. 1). The temperature of the catalyst support was controlled within $\pm$ 2° C. by the use of either a Hoskins RM type temperature controller or a Foxboro potentiometer type controller.

Ethylene Purity

The ethylene obtained in cylinders from the Ohio Chemical Company was derived from alcohol and was "99.5% USP". Samples from two cylinders analyzed at the U.S. Bureau of Standards with the mass spectrometer were both found to contain the following impurities: air, butene-2, *n*-pentane, and diethyl ether. Methane and ethane supplied from the same source were claimed by the manufacturer to be of 90% and 95% purity respectively and were not analyzed. The propane used was a commercial grade of approximately 98% purity.

Analytical Methods

In the experiments reported, ethylene oxide, carbon dioxide, and water were the only products of the reaction.

The ethylene content of the hydrocarbon–air mixture used, and of the product, was determined in our early work by absorption in fuming sulphuric acid in an Orsat type gas analysis apparatus, using mercury as confining liquid. More recently a sodium nitrate–mercuric nitrate–nitric acid solution (8) has been found to be a more convenient reagent.

Ethylene oxide was determined by scrubbing the off-gas (or a measured fraction thereof) at a rate not exceeding 120 liters per hour for 5 to 10 min. through the absorption tower, *B* (Fig. 2), containing 20 to 50 cc. of 0.1 to 0.6 *N* hydrochloric acid saturated with magnesium chloride. Ethylene oxide reacts quantitatively with such a solution to form ethylene chlorhydrin (14, 23):

$$C_2H_4O + HCl \longrightarrow ClCH_2CH_2OH$$

and was determined by titration of the residual free acid with 0.1 to 0.4 *N* sodium hydroxide solution, using methyl orange–indigo carmine indicator. The accuracy of this method for determining ethylene oxide in the off-gas

was confirmed by scrubbing the off-gas through dilute sulphuric (0.5 to 2%) at 70° C. Under these conditions ethylene oxide is quantitatively converted to mono- and diethylene glycol. After neutralization of the sulphuric acid the glycols were recovered by fractionation.

A rough estimate of the amount of ethylene oxide in the off-gas could be rapidly and conveniently made by bubbling the off-gas through 2 cc. of the hydrochloric acid–magnesium chloride reagent (containing one drop of the methyl orange–indigo carmine indicator) in a test tube and noting the time taken for the indicator to change color.

The carbon dioxide in the off-gas was determined by an absorption method similar to that used for the ethylene oxide determination. The off-gas (or a measured fraction thereof) was scrubbed at a rate not exceeding about 120 liters per hour for three to five minutes through 100 cc. of 0.1 to 0.4 *N* sodium hydroxide solution, and the carbon dioxide was determined by addition of excess barium chloride and titration of the residual caustic with 0.1 to 0.6 *N* hydrochloric acid, using phenolphthalein as indicator. This is a modification of the method described by W. B. Brown (4).

Results

Effect of Temperature on the Promoted and on the Unpromoted Catalyst

The effect of temperature on the per cent conversion of ethylene to ethylene oxide per pass, and on the selectivity, is shown in Fig. 3 and Table II for pure silver, silver + 1.3% calcium oxalate, and silver + 1.3% calcium oxalate + 2% stannous oxide over the range 260-350° C.

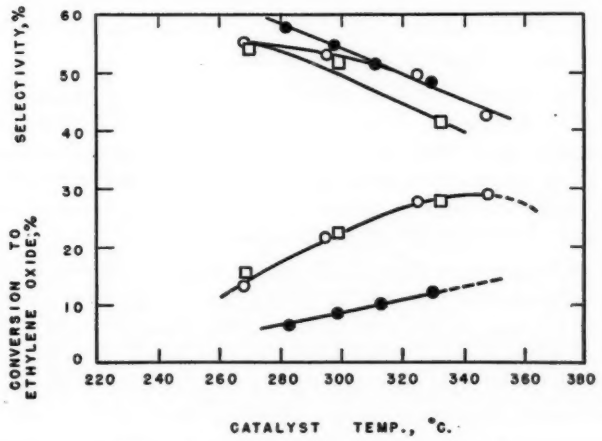

FIG. 3.—*Effect of temperature on conversion and selectivity.*
● *pure silver,* ○ *silver + 1.3% calcium oxalate,*
□ *silver + 1.3% calcium oxalate + 2% stannous oxide.*

TABLE II

EFFECT OF TEMPERATURE ON CONVERSION AND ON SELECTIVITY

One-inch stainless steel reaction tube; "star" silver support. Area = 106 cm.²; ethylene 5.4 liters per hr.; air, 81 liters per hr. (22° C., 760 mm.); time of contact (300° C.) = 1.3 sec. Tests made after catalyst had been conditioned for 24 hr. at 300° C.

Catalyst	Catalyst temperature, °C.	Conversion of ethylene to ethylene oxide, %	Selectivity, %
Pure silver	282	7.6	58.0
	298	9.2	55.0
	312	10.8	51.0
	329	12.7	48.5
Silver + 1.3% calcium oxalate	268	14.1	55.5
	295	21.9	53.0
	325	27.9	49.5
	348	29.1	42.5
Silver + 1.3% calcium oxalate + 2% stannous oxide	268	16.0	55.0
	298	23.1	51.5
	332	28.1	41.0

As shown in Fig. 3, the promoted catalysts gave much higher conversions, accompanied by somewhat lower selectivity, than the pure silver. The addition of 2% stannous oxide to the silver–calcium oxalate catalyst had no appreciable effect on the per cent conversion of ethylene to ethylene oxide per pass. Whereas the pure silver catalyst showed appreciable signs of sintering after 24 hr. at 300° C., catalysts promoted with calcium oxalate and stannous oxide have been used continuously for six weeks at that temperature without any decrease in activity or any sintering visible under the microscope.

Effect of Air Ethylene Ratio and of Time of Contact

The results of Expts. 1 to 9, as listed in Table III and plotted in Fig. 4, show the effect of varying the air–ethylene ratio on the conversion of ethylene to ethylene oxide and on the selectivity. These single-pass experiments were made with the 1 in. stainless steel reaction tube containing 15 silver disks coated with a silver catalyst containing 1.3% calcium oxalate and 2% stannous oxide. The catalyst temperature was 302° C.

At the three ethylene rates used, beginning with an air–ethylene ratio of 5/1 or less, increasing the air–ethylene ratio by increasing the air rate (and total flow rate) caused an initial increase in both selectivity and conversion. After an air–ethylene ratio of about 10/1 was reached in each case, doubling the air–ethylene ratio (and approximately halving the time of contact) by doubling the air flow rate had almost no effect on the conversion or selectivity.

Fig. 4 shows that for the same air–ethylene ratio a slight improvement in selectivity was observed as the time of contact was decreased, this effect of time of contact on selectivity being less pronounced at low air–ethylene

TABLE III

EFFECT OF VARYING AIR–ETHYLENE RATIO AND TIME OF CONTACT ON CONVERSION TO ETHYLENE OXIDE AND ON SELECTIVITY

Run No.	Ethylene input, liters/hr.*	Air input, liters/hr.*	Air–ethylene	Time of contact, sec.**	Conversion of ethylene to ethylene oxide, %	Total ethylene reacted, %	Selectivity %
1	2.8	13	4.6	2.1	25.0	53.0	47.5
2	2.8	25	8.9	1.2	32.5	66.0	49.5
3	2.8	52	18.5	0.6	34.5	68.5	50.5
4	5.6	25	4.5	1.1	22.5	46.5	48.5
5	5.6	52	9.3	0.6	25.5	49.0	52.0
6	5.6	104	18.5	0.3	25.5	48.0	53.0
7	12.0	25	2.1	0.9	9.2	21.7	42.5
8	12.0	52	4.3	0.5	15.0	31.0	48.5
9	12.0	104	8.7	0.3	17.5	34.0	51.0
10	8.4	78	9.3	0.4	21.0	43.0	50.5

* *At 22° C., 760 mm.*
** *At 302° C.*

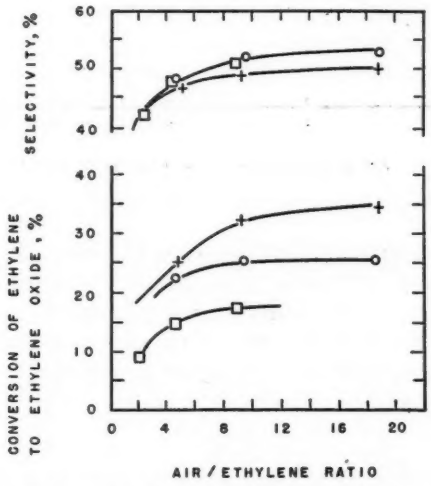

FIG. 4. *Effect of varying the air–ethylene ratio.*
\+ *2.8 liters/hr. ethylene,*
○ *5.6 liters/hr. ethylene,*
□ *12.0 liters/hr. ethylene.*

ratios. In Fig. 5, log total liters per hr. of ethylene reacted is plotted against log average ethylene rate for all runs where the air–ethylene ratio was greater than 5/1. The slope of the straight line through the points is 0.48; this indicates that the total reaction rate was approximately proportional to the square root of the average ethylene flow rate. It follows, therefore, that at a

constant air rate when air is in large excess the rate of reaction is proportional to the square root of the ethylene concentration.

This relation between the reaction rate and the ethylene concentration is similar to the relation observed by Benton and Elgin (2) and Benton (1) between the reaction rate and hydrogen concentration in their investigation

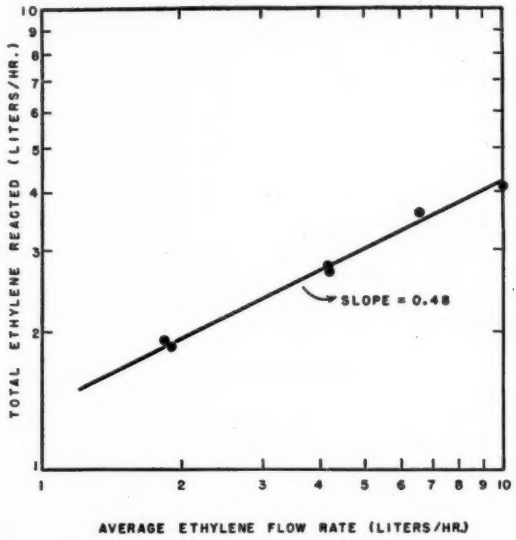

FIG. 5. *Relation between total reaction rate and average ethylene flow rate.*

of the combination of hydrogen and oxygen over silver. Thus, the oxidation of ethylene on silver would appear to be another example of the special case discussed in the latter paper, involving two reacting gases one of which is strongly adsorbed, the reaction product being also strongly adsorbed and reaction rate being proportional to the square root of the concentration of the gas that is not adsorbed.

Ethylene in Excess

The experiments reported in Table IV were made with the 1 in. stainless steel reaction tube and the "star" silver support (Fig. 1). Two grams of catalyst (silver + 1.3% calcium oxalate + 2% stannous oxide) was used and the catalyst temperature throughout the runs was 270° C. It will be noted that the selectivities are low and decrease with decreasing oxygen–ethylene ratio—in agreement with predictions based on the earlier results reported in Table III. In the runs with ethylene in excess, the rate of reaction was approximately proportional to the oxygen concentration. Nitrogen dilution at a 4/1 nitrogen-oxygen ratio had little effect on the rate of reaction or selectivity. For comparison the selectivity obtained in a run at 268° C.

TABLE IV

ETHYLENE IN EXCESS

Ethylene, liters/hr.*	Nitrogen, liters/hr.*	Oxygen, liters/hr.	Oxygen/ ethylene	Time of contact, sec.	Total ethylene reacted, %	Selectivity, %
50	20	5.2	0.104	1.3	3.6	34
50	—	4.9	0.098	1.8	3.8	33.5
50	—	2.23	0.045	1.9	1.8	25
5.0	59	15.7	3.1	1.3	29	55**

** 0° C., 760 mm.*

*** Air in excess; these figures were taken from Table II for comparison.*

with oxygen in excess has been taken from Table II and entered at the bottom of Table IV. It will be noted that the selectivity increases from about 25% of the total ethylene reacted with ethylene in large excess to about 55% with oxygen in large excess.

Effect of Paraffins and Propane

It has been observed that the addition of methane and ethane and, to a more marked degree, propane to the ethylene-air mixture caused a depression in the rate of conversion of ethylene to ethylene oxide, an effect that persisted after the addition of the paraffin was stopped. In fact, it took several days of continuous operation with pure ethylene before the initial conversion rate was re-established. Simultaneously with the decrease in per cent conversion to ethylene oxide, the apparent rate of conversion of ethylene to carbon dioxide and water, as indicated by the selectivity, showed a marked increase. The results of several experiments are given in Table V and plotted in Fig. 6.

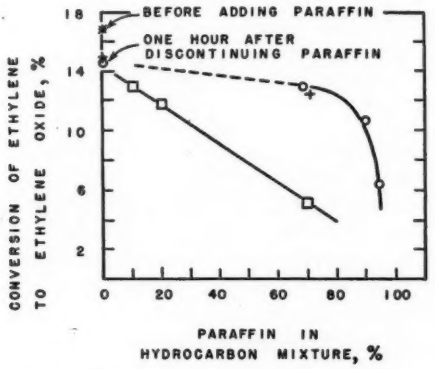

FIG. 6. *Effect of methane, ethane, and propane.* + *methane–ethylene,* ○ *ethane–ethylene,* □ *propane–ethylene.*

TABLE V

EFFECT OF METHANE, ETHANE, AND PROPANE IN THE ETHYLENE FEED ON CONVERSION TO ETHYLENE OXIDE AND ON SELECTIVITY

One-inch stainless steel reaction tube; 15 silver disks; area, 135 cm.²; 277° C.; 1 atm.; catalyst, silver + 1.3% calcium oxalate + 2% stannous oxide; air/ethylene, 10-19.

Expt. No.	Ethylene + paraffin, liters/hr.*	Ethylene, liters/hr.*	% paraffin in hydrocarbon gas	Air, liters/hr.*	Conversion of ethylene to ethylene oxide, %	Selectivity,** %
Before adding paraffins						
1	5.4	5.4	0	52	17.0	57.5
Ethylene-methane						
2	18.3	5.3	71	52	12.6	29.5
3	5.4	5.4	0	52	14.7†	34†
Ethylene-ethane						
4	102	5.5	95	52	6.2	15
5	50	5.2	90	104	10.5	25
6	18.2	5.5	70	52	12.9	32
7	5.3	5.3	0	52	14.5†	34†
Ethylene-propane						
8	18.5	5.5	70	104	5.1	—
9	6.8	5.4	20	52	11.8	—
10	6.0	5.4	10	52	13.1	—

* *22° C., 1 atm.*

** *Uncorrected for paraffin oxidation.*

† *One hour after discontinuing paraffin.*

The above effect has been observed both with the unpromoted and the promoted catalyst.

Effect of Ethylene Dichloride

In experiments with 99.5% ethylene the addition of ethylene dichloride was tried in an attempt to improve the selectivity of the catalyst. It was found, however, that when the dichloride was added in amounts as low as 0.0001% of the inlet gas volume, the catalyst was rapidly poisoned. It was interesting to note that the activity of a catalyst, after it had been poisoned almost completely by this method, could be largely and rapidly restored by the addition of a controlled amount of methane or ethane in the inlet feed gas.

Our experiments suggest that the beneficial effect claimed by Berl (3) and by Law and Chitwood (19) is dependent on the presence of paraffins in the ethylene–air mixture.

Acknowledgment

The assistance of W. A. Tidridge in repeating some of the original work on the effect of temperature on catalyst activity and on the effect of using a high ethylene–air ratio is gratefully acknowledged by the authors.

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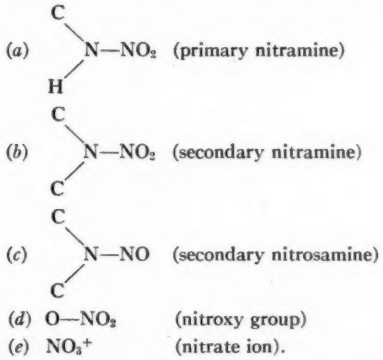
THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC NITRAMINES, NITROSAMINES, AND NITRATES[1]

By R. Norman Jones and G. Denis Thorn

Abstract

The ultraviolet absorption bands associated with the following groups have been investigated in a variety of compounds of known structure:



The groups may be characterized by the ultraviolet spectrum, and the number of each type of group present in a given compound may be estimated from an analysis of the shape and intensity of the absorption spectrum. These correlations have been applied to the elucidation of the structure of new compounds isolated in the course of the investigation of the chemistry of 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX).

I. Introduction

In this paper the ultraviolet absorption spectra of some 60 aliphatic nitrogen compounds are recorded. These measurements were made as part of a co-operative investigation of the chemistry of the explosive 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (VII). Many of the compounds examined are intermediates and by-products that were obtained at the University of Toronto and at McGill University during the course of studies on the mechanism of formation of RDX by the Bachmann process. The structures of some of the substances are based on indirect evidence only, and the spectra provided a link in the chain of evidence leading to the structural formulas finally accepted.

In connection with this work, Dr. A. Blomquist kindly made available to us a considerable number of nitramines and derivatives which had been

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This paper is based on a series of reports submitted to the Associate Committee on Explosives of the National Research Council between November 30, 1942 and August 10, 1944. The manuscript was cleared for publication on April 24, 1948.

prepared at Cornell University by unequivocal methods of synthesis, (4) and these compounds were of great value in establishing empirical relations between structure and spectra. Other compounds were supplied also by Dr. C. B. Purves of McGill University, Dr. W. E. Bachmann of the University of Michigan, Dean F. C. Whitmore and Dr. C. I. Noll of Pennsylvania State College, and Dr. M. Carmack of the University of Pennsylvania.

The spectrographic literature contains only meager references to aliphatic nitrogen containing compounds. Baly and Desch (2), and Hedley (18) in 1908 described the spectra of a few such compounds. Hantzsch and Hein (14) reported on the spectra of several nitro compounds and their alkali salts in 1919 and, more recently, Kortüm has discussed the spectra of several aliphatic nitrogen containing compounds (20–22) including a few simple nitramines (22).

In Table I, references are listed to the published work on the spectra of nitramines, nitrosamines, nitrosohydroxylamines, nitrate and nitrite esters, nitroxy, and nitroso compounds of interest in connection with the chemistry of explosives.

TABLE I

REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS

Formula	Compound	Alternative names and symbolic designations	References*
$H_2N_2O_2$	Nitramide	Nitramine	2, 22, *
$H_2N_2O_3$	Nitrohydroxylamine		22
$H_4N_2O_3$	Ammonium nitrate		19
CN_4O_8	Tetranitromethane		16, 21
CHN_3O_6	Trinitromethane		14, 21
CH_2NO_2Br	Bromonitromethane		18
$CH_2N_2O_4$	Dinitromethane		14, 18, 21
CH_3NO_2	Mononitromethane		2, 10
CH_3NO_2	Methyl nitrite		26
$CH_3N_3O_3$	Mononitrourea	Nitrocarbamide	2
$CH_4N_2O_2$	N-Methylnitrosohydroxylamine		22
$CH_4N_2O_2$	Methylnitramine		2, 6, 9, 22
$CH_4N_4O_2$	Nitroguanidine	Picrite	2, 8
$CH_4N_4O_4$	Methylenedinitramine		6, *
$CH_4N_4O_4$	Methylene-*bis*-nitrosohydroxylamine	"Traube Compound"	9, *
$C_2H_5NO_2$	Nitrosoethane	Ethyl nitrite	10, 16, 26
$C_2H_5NO_3$	Nitroxyethane	Ethyl nitrate	10, 11, 17, 26, *
$C_2H_5N_3O_5$	1-Nitroxy-2-nitro-2-azapropane		*
$C_2H_5N_3O_5$	1-Nitroxy-3-nitro-3-azapropane	2-Nitroxy ethylnitramine NENA	*
$C_2H_6N_2O$	Dimethylnitrosamine		2, 5, 9, *
$C_2H_6N_2O_2$	Dimethylnitramine		9, 22
$C_2H_6N_2O_2$	Ethylnitramine		22
$C_2H_6N_4O_4$	Ethylenedinitramine	EDNA	6, 8

** The numerical references relate to the publications listed in the bibliography on page 860. The symbol * in this column indicates that the spectrum of the compound is described in this article.*

The preparation and chemical properties of certain of the compounds included in this table have not yet been described fully in the literature (see Introduction, page 828).

TABLE I—*Continued*

REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS—*Continued*

Formula	Compound	Alternative names and symbolic designations	References *
$C_2H_{10}N_4O_6$	Ethylenediamine dinitrate		*
$C_3H_4N_4O_5$	2,5-Dinitro-2,5-diazacyclopentanone-1	Dinitroethyleneurea	*
$C_3H_6N_2O_3$	Nitrosourethane		2
$C_3H_6N_2O_4$	Nitrourethane		2, *
$C_3H_6N_4O_5$	1-Oxa-3,5-dinitro-3,5-diazacyclohexane	Cyclonite oxide	*
$C_3H_6N_6O_3$	1,3,5-Trinitroso-1,3,5-triazacyclohexane	Trinitrosotrimethylenetriamine	9, *
$C_3H_6N_6O_5$	1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane	NOX	9, *
$C_3H_6N_6O_6$	1,3,5-Trinitro-1,3,5-triazacyclohexane	Trinitrotrimethylenetriamine. RDX	8, 9, 24, *
$C_3H_7N_3O_5$	1-Nitroxy-3-nitro-3-azabutane		*
$C_3H_7N_3O_7$	1,5-Dinitro-3-nitroxy-1,5-diazapentane		*
$C_3H_8N_4O_4$	1,5-Dinitro-1,5-diazapentane	1,3-Propylenedinitramine	6
$C_3H_8N_4O_4$	1,4-Dinitro-1,4-diazapentane		*
$C_3H_8N_4O_4$	1,4-Dinitro-2-methyl-1,4-diazabutane		*
$C_3H_8N_4O_4$	Methylene-*bis*-nitrosohydroxylamine α-methyl ester	Traube Compound α-methyl ester	9, *
$C_3H_8N_4O_4$	Methylene-*bis*-nitrosohydroxylamine β-methyl ester	Traube Compound β-methyl ester	9, *
$C_3H_8N_6O_7$	1,3-Dinitro-1,3,5-triazacyclohexane-5-nitrate	PCX	*
$C_4H_8N_2O_3$	1-Oxa-4-nitro-4-azacyclohexane	N-Nitromorpholine	*
$C_4H_8N_4O_3$	1-Nitro-4-nitroso-1,4-diazacyclohexane	N-Nitro-N′-nitrosopiperazine	*
$C_4H_8N_4O_4$	1,4-Dinitro-1,4-diazacyclohexane	N,N′-Dinitropiperazine	*
$C_4H_8N_4O_8$	1,5-Dinitroxy-3-nitro-3-azapentane	DINA	*
$C_4H_8N_6O_6$	1,3,5-Trinitro-1,3,5-triazacycloheptane	Hept.-RDX	*
$C_4H_8N_6O_6Cl_2$	1,7-Dichloro-2,4,6-trinitro-2,4,6-triazaheptane	GSX	*
$C_4H_8N_8O_7$	1-Nitroso-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane	N-HMX	*
$C_4H_8N_8O_8$	1,3,5,7-Tetranitro-1,3,5,7-tetrazacycloöctane	HMX	9, *
C_4H_9NO	*tert*-Nitrosobutane		2
$C_4H_9N_5O_5$	1,3-Dinitro-5-methylol-1,3,5-triazacyclohexane		9
$C_4H_9N_6O_6Cl$	1-Chloro-2,4,6-trinitro-2,4,6-triazaheptane	OFX	*
$C_4H_{10}N_2O$	Diethylnitrosamine		2
$C_4H_{10}N_2O_2$	*n*-Butylnitramine		*
$C_4H_{10}N_2O_5$	N-(Trimethylolmethyl)-nitrosohydroxylamine		6
$C_4H_{10}N_2O_5$	N-(Trimethylolmethyl)-nitramine		6
$C_4H_{10}N_4O_4$	2,5-Dinitro-2,5-diazahexane	N,N′-Dimethyl EDNA	*
$C_4H_{10}N_4O_9$	1,5-Dinitroxy-3-azapentane nitrate		*

TABLE I—*Continued*

REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS—*Continued*

Formula	Compound	Altenrative names and symbolic designations	References *
$C_4H_{11}N_5O_4$	1,7-Dinitro-1,4,7-triazaheptane		*
$C_4H_{13}N_5O_9$	1-Nitroxy-3,6-diazahexane dinitrate		*
$C_5H_4N_2O_3$	Furfural nitramide		*
$C_5H_8N_4O_{12}$	Pentaerythratol tetranitrate	PETN	24
$C_5H_9NO_2$	2-Methyl-2-nitrosobutanone-3	*tert*-Nitrosoisopropyl-acetone	2, 13
$C_6H_9N_3O_5$	1-Acetyl-3,5-dinitro-1,3,5-triaza-cyclohexane	TAX	*
$C_6H_{10}N_6O_2$	Dinitrosopentamethylenetetra-mine		*
$C_5H_{10}N_6O_4$	Dinitropentamethylenetetramine	DPT	8, *
$C_5H_{10}N_{10}O_{14}$	1,9-Dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	"106"	*
$C_5H_{11}NO_2$	*n*-Amyl nitrite		2, 5, 9
$C_5H_{11}N_3O_4$	1,5-Dinitro-3-methyl-1,3,5-tri-azacycloheptane		*
$C_5H_{11}N_5O_7$	2,5-Dinitro-7-nitroxy-2,5-diaza-heptane		*
$C_5H_{12}N_6O_6$	1,5-Dinitro-3-methyl-3-(methyl-enenitramine)-1,5-diazapen-tane	PGX	*
$C_5H_{12}N_6O_7$	1-Methoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methoxy-MSX	*
$C_5H_{12}N_3O_4$	2,6-Dinitro-4-methyl-2,4,6-triazaheptane		*
$C_6H_{11}N_7O_7$	1-Acetyl-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane	SEX (QDX)	*
$C_6H_{12}N_6O_8$	1-Acetoxy-2,4,6-trinitro-2,4,6-triazaheptane	MSX	*
$C_6H_{12}N_6O_{10}$	1,8-Dinitroxy-3,6-dinitro-3,6-diazaoctane		*
$C_6H_{13}N_3O_8$	Hexamethylenetetramine mono-nitrate		*
$C_6H_{14}N_2O_2$	Cyclohexylamine nitrite		9
$C_6H_{14}N_4O_9$	2,6-Dinitroxy-4-azaheptane nitrate		*
$C_6H_{14}N_6O_6$	Hexamethylenetetramine dini-trate		*
$C_6H_{14}N_6O_7$	1-Ethoxy-2,4,6-trinitro-2,4,6-triazaheptane	Ethoxy-MSX	*
$C_6H_{16}N_6O_{12}$	1,8-Dinitroxy-3,6-diazaoctane dinitrate		*
$C_6H_{18}N_6O_4Cl_2$	1,10-Dinitro-1,4,7,10-tetrazade-cane 4,7-dihydrochloride		*
$C_6H_{18}N_8O_{10}$	1,10-Dinitro-1,4,7,10-tetrazade-cane 4,7-dinitrate		*
$C_7H_{13}NO_8$	α-Methyl-D-glucose-6-nitrate		*
$C_7H_{15}N_5O_6$	1,7-Dinitro-4-carboethoxy-1,4,7-triazaheptane		*
$C_8H_{14}N_4O_8$	1,4-Dicarboethoxy-1,4-dinitro-1,4-diazabutane	Ethylene-*bis*-nitrourethane	*

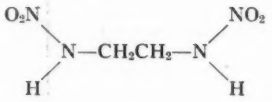
TABLE I—*Concluded*

REFERENCES TO THE ULTRAVIOLET ABSORPTION SPECTRA OF ALIPHATIC EXPLOSIVES AND RELATED COMPOUNDS—*Concluded*

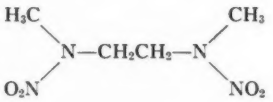
Formula	Compound	Alternative names and symbolic designations	References *
$C_8H_{14}N_6O_{10}$	1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane	BSX	*
$C_8H_{17}NO_2$	2-Nitroöctane		25
$C_8H_{17}NO_2$	2-Octyl nitrite		23
$C_8H_{18}N_8O_8$	$\Delta^{5,6}$-2,10,13-Trinitro-6-oxo-7-oxa-2,5,6,10,13-pentazatetradecane		*
$C_8H_{20}N_2O_3$	Tetraethylammonium nitrate		12, 20
$C_9H_{16}N_8O_{12}$	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	AcAN	*
$C_9H_{18}N_6O_4$	N-Acetylaminomethylhexamethylenetetramine mononitrate	H_2	*
$C_9H_{18}N_{10}O_8$	Methylene-*bis*-3,6-dinitro-1,3,6-triazacycloheptane		*
$C_{10}H_{19}NO_8$	2,3,4-Trimethyl-β-methyl-D-glucose-6-nitrate		*
$C_{11}H_{19}N_7O_{11}$	1,9-Diacetoxy-2,4,8-trinitro-6-acetyl-2,4,6,8-tetrazanonane	H_{16}	*
$C_{12}H_{24}N_6O_8$	1,10-Dinitro-4,7-dicarboethoxy-1,4,7,10-tetrazadecane		*
$C_{12}H_{28}N_2O_3$	Tetrapropylammonium nitrate		12
$C_{13}H_{19}NO_{11}$	2,3,4-Triacetyl-α-methyl-D-glucose-6-nitrate		*
$C_{13}H_{19}NO_{11}$	3,4,6-Triacetyl-β-methyl-D-glucose-2-nitrate		*

II. The Spectra of Nitramines

The spectra of aqueous, alcoholic, or dioxane solutions of both primary and secondary nitramines are relatively simple. One broad structureless band is present, with a maximum in the region between 2250 and 2400 Å. The spectrum of a typical primary nitramine, ethylenedinitramine (I), is given in Fig. 1 and that of a typical secondary nitramine, 2, 5-dinitro-2,5-diazahexane (II)*, in Fig. 2.



I



II

* *The nomenclature adopted in this article has not been rigidly systematized. For the simpler compounds, the names in common use have been employed, i.e., "methylnitramine". For compounds of more complex structure the systematic "aza" nomenclature has been employed. As applied to heterocyclic compounds, this is described by Patterson, (J. Am. Chem. Soc. 55:3905. 1933); its extension to linear compounds follows logically. In the interests of brevity we have occasionally retained certain of the abbreviations (RDX, DPT, etc.) favored by explosives chemists, where it seemed advantageous to do so; these trivial names and symbolic designations are cross-referenced with the systematic names in Table I.*

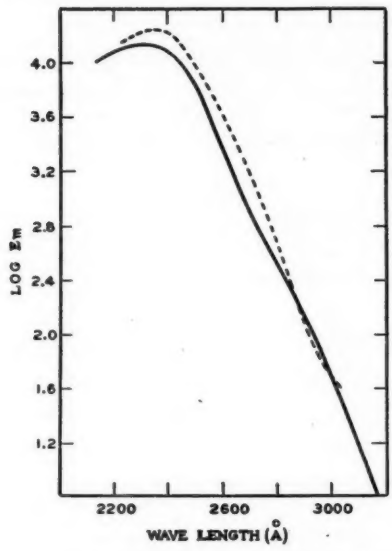


FIG. 1. *Spectrum of typical primary nitramine (Ethylenedinitramine).*
———— *Curve A. Solvent, ethanol.*
- - - - - - - - - - - *Curve B. " 0.2 N sodium hydroxide.*

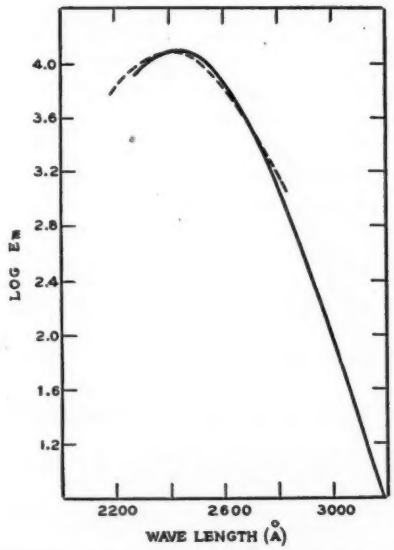


FIG. 2. *Spectrum of typical secondary nitramine (2,5-dinitro-2,5-diazahexane).*
———— *Curve A. Solvent, dioxane.*
- - - - - - - - - - - *Curve B. " 0.2 N sodium hydroxide.*

A. Secondary Nitramines

The wave lengths and intensities of the absorption maxima of a number of secondary nitramines are listed in Table II. For compounds containing one nitramine group per molecule the molecular extinction coefficient at the maximum (E_{max}) is close to 5500. It is observed empirically that in the

TABLE II

ABSORPTION SPECTRA OF SECONDARY NITRAMINES
WAVE LENGTH AND INTENSITY OF THE MAXIMUM

Structure	Compound	Solvent	Absorption Max.		$\frac{E_{max}}{5500}$
			λ, Å	E_{max}	
	N-nitromorpholine	Ethanol	2470	5400	0.98
	Dimethylnitramine	Dioxane	2400	6300	1.14
XL	1,5-Dinitroxy-3-nitro-3-azapentane	Ethanol Dioxane	2350 2330	6770 7330	1.23* 1.34
XXXVIII	1-Nitroxy-2-nitro-2-azapropane	Ethanol	2380	6710	1.22*
XIV	Dinitropentamethylenetetramine	Dioxane	2410	11000	2.00
	Dinitropiperazine	Dioxane	2500	11000	2.00
XVIII	1,3-Dinitro-1,3,5-triazacyclohexane-5-nitrate	Dioxane	2350	11320	2.06
XVI	1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane	Ethanol Dioxane	2240 2240	6230 6450	1.13† 1.17
IX	3,5-Dinitro-1-oxa-3,5-diazacyclohexane	Ethanol	No maximum		
	Dinitroethyleneurea	Ethanol	2460	10500	1.91
II	2,5-Dinitro-2,5-diazahexane	Dioxane	2410	12250	2.21
XXXVII	2,5-Dinitro-7-nitroxy-2,5-diazaheptane	Dioxane	2410	11850	2.15*
XXXIX	1,8-Dinitroxy-3,6-dinitro-3,6-diazaoctane	Dioxane	2390	12200	2.22*
XXVI	1,4-Dicarboethoxy-1,4-dinitro-1,4-diazabutane	Dioxane	2350	10250	1.86
	2,6-Dinitro-4-methyl-2,4,6-triazaheptane	Ethanol	2290	13570	2.44
	1,5-Dinitro-3-methyl-1,3,5-triazacycloheptane	Ethanol	2325	13000	2.35
	1,7-Diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane	Ethanol	2280	17000	3.09
XVII	1-Acetyl-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane	Ethanol	2280	17800	3.24

* *The high value for $E_{max}/5500$ in these compounds is probably associated with the presence of the nitroxy group and is discussed on page 856.*

† *See discussion on page 843.*

TABLE II—*Concluded*

ABSORPTION SPECTRA OF SECONDARY NITRAMINES
WAVE LENGTH AND INTENSITY OF THE MAXIMUM—*Concluded*

Structure	Compound	Solvent	Absorption Max.		$\frac{E_{max}}{5500}$
			λ, Å	E_{max}	
	1-Methoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methanol	2350	16200	2.95
	1-Ethoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methanol	2350	16600	3.02
	1-Acetoxy-2,4,6-trinitro-2,4,6-triazaheptane	Methanol	2320	16600	3.02
	1-Chloro-2,4,6-trinitro-2,4,6-triazaheptane	Dioxane	2330	17400	3.16
	1,7-Dichloro-2,4,6-trinitro-2,4,6-triazaheptane	Dioxane	2310	18200	3.30
VII	1,3,5-Trinitro-1,3,5-triazacyclohexane	Ethanol	No maximum		
XIII	1,3,5-Trinitro-1,3,5-triazacycloheptane	Ethanol	2330	14900	2.72
	$\Delta^{5,6}$-2,10,13-trinitro-6-oxo-7-oxa-2,5,6,10,13-pentazatetradecene	Dioxane	2410	20100	3.66
XLI	1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	Dioxane	2320	21900	3.98
XXXVI	1,9-Dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane	Dioxane	2280	21850	3.97
VIII	1,3,5,7-Tetranitro-1,3,5,7-tetrazacycloöctane	Ethanol	2280	21400	3.90
	Methylene-*bis*-3,6-dinitro-1,3,6-triazacycloheptane	Ethanol	2340	23400	4.25

absence of secondary complicating factors E_{max} increases in direct proportion to the number of nitramine groups in the molecule, so that for a substance containing n secondary nitramine groups the molecular extinction coefficient at the maximum is close to $5500 \times n$. This is illustrated in Column 6 of Table II in which E_{max} is divided by 5500. We propose to call this factor the *molecular extinction constant* of the secondary nitramine group**.

** *Linear relations of this kind, correlating the molecular extinction coefficient at a maximum with the frequency of occurrence of a certain chromophore in a molecule, have not previously been established for any extensive series of compounds and the term molecular extinction constant has not hitherto been used in spectrographic literature. In the general case it may be defined in the following terms. If, in a series of compounds, each of which contains n identical chromophoric groups, the molecular extinction coefficient at the wave length* $\lambda(E_\lambda)$ *can be represented by the equation*

$$E_\lambda = nC_\lambda$$

C_λ *is the molecular extinction constant of the chromophoric group for the wave length* λ.

B. Primary Nitramines

In Table III the absorption data are given for a number of primary nitramines in water, alcohol, or dioxane. Here also a linear relation between the intensity of E_{max} and the number of nitramine groups in the molecule is observed. The molecular extinction constant for the primary nitramine group at the maximum in neutral solution is 7000. One compound has been examined which contains both a primary and a secondary nitramine group, and in this case (III) the observed extinction coefficient agrees well with that calculated by summation of the molecular extinction constants for one primary

TABLE III

ABSORPTION SPECTRA OF PRIMARY NITRAMINES
WAVE LENGTH AND INTENSITY OF THE MAXIMUM

Structure	Compound	Solvent	Absorption max.		$\frac{E_{max}}{7000}$
			λ, Å	E_{max}	
	Nitramide	Water	2250	5900	0.84
	Methylnitramine	5×10^{-3} *N* HCl	2325	7200	1.03*
XXII	N-(trimethylolmethyl)-nitramine	Water	2350	6970	1.00†
	n-Butylnitramine	Ethanol	2325	7200	1.03
VI	2-Nitroxyethylnitramine	Ethanol	2240	5500	0.80
I	Ethylenedinitramine	Ethanol	2300	13400	1.92
	1,7-Dinitro-1,4,7-triazaheptane	0.2 *N* HCl	2280	13970	2.00
XIX	Methylenedinitramine	Ethanol	2260	12530	1.80
IV	1,10-Dinitro-4,7-dicarboethoxy-1,4,7,10-tetrazadecane	Dioxane	2350	11500	1.65‡
V	1,7-Dinitro-4-carboethoxy-1,4,7-triazaheptane	Dioxane	2340	11200	1.60‡
XLII	1,10-Dinitro-1,4,7,10-tetrazadecane-4,7-dinitrate	Water	Inflection only		
XLIII	1,10-Dinitro-1,4,7,10-tetrazadecane-4,7-dihydrochloride	Water	2300	15970	2.28
	1,4-Dinitro-2-methyl-1,4-diazabutane	Ethanol	2350	13400	1.92
	1,5-Dinitro-3-nitroxy-1,5-diazapentane	Dioxane	2275	14450	2.06
	1,5-Dinitro-3-methyl-3-(methylenenitramine)-1,5-diazapentane	Ethanol	2350	23800	3.39

* *Data taken from measurements of Kortüm (21).*

† *Data privately communicated by Dr. Carmack (See also references (6, 7)).*

‡ *See page 849.*

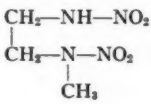
and one secondary group. The ratio of the predicted to the observed maximal molecular extinction coefficient of this compound is shown in the right hand

TABLE IV

ABSORPTION SPECTRA OF MIXED PRIMARY AND SECONDARY NITRAMINES
POSITION AND INTENSITY OF THE MAXIMA

Structure	Compound	Solvent	Absorption max.		E_{max} obs. / E_{max} predicted
			λ, Å	E_{max} obs.	
III	1,4-Dinitro-1,4-diazapentane	Ethanol	2375	12950	1.04
	Potassium salt of III	0.2 *N* HCl	2360	12200	0.99

column of Table IV. It should be noted that in the nitramines E_{max} is closely the same in both ethanol and dioxane solutions.



III

The majority of both the primary and secondary nitramines that were available to us contained additional functional groups and the influence of these groups must be taken into consideration in evaluating the spectrometric data. It is well known that in compounds containing more than one chromophoric group the different chromophores will absorb more or less independently of one another, provided they are separated by at least one methylene group. In such compounds the observed absorption approximates closely to that which would be predicted from the sum of the absorptions associated with the separate chromophores.

In Tables II, III, and IV are included all primary and secondary nitramines in which the other nonconjugated functional substituents do not appear to influence the shape of the spectral curve. These substituents are summarized in Table V. It cannot be assumed, however, that these substituents will necessarily show no effects on the spectra of other nitramines; this may depend on the ratio of the number of such groups to the number of nitramine groups in the molecule. In the case of compounds containing the nitroxy group (–C–O–NO_2), together with nitramine groups, increases in the intensity of absorption at the nitramine maximum are observed that can be attributed to the effect of the nitroxy absorption (page 852). It is probable that some of the deviations from whole numbers in Column 6 of Tables II and III may be due to similar causes (page 857).

TABLE V

SUBSTITUENT GROUPS (R) WHICH MAY BE INTRODUCED INTO THE MOLECULES $R{-}CH_2{-}NH{-}NO_2$ AND $R{-}CH_2{>}N{-}NO_2$ $R{-}CH_2$ WITHOUT SIGNIFICANTLY ALTERING THE SHAPE OF THE SPECTRAL CURVE

1. $-O-COCH_3$	7. $-N(COCH_3)-$
2. $-O-NO_2$	8. $-N(COOC_2H_5)-$
3. $NH_2^+ NO_3^-$	9. $-NH_2^+ Cl^-$
4. $-Cl$	
5. $-OCH_3$	
6. $-OC_2H_5$	

C. Spectra of Nitramines in Alkaline Solution

The hydrogen atom attached to nitrogen in the primary nitramine group has acidic properties, and it is therefore to be anticipated that in alkaline solution the spectrum of a primary nitramine may show a change attributable to the effect of ionization.

The spectra of several primary nitramines have been determined in the presence of sodium hydroxide solution (Table VI). The absorption spectrum

TABLE VI

ABSORPTION SPECTRA OF PRIMARY NITRAMINES IN ALKALINE SOLUTION

Structure	Compound	Solvent	Absorption max.		$\frac{E_{max}}{8500}$
			λ, Å	E_{max}	
	Methylnitramine	*N*/4 KOH	2280	7600	0.90*
XXII	N-(trimethylolmethyl)-nitramine	*N* NaOH	2360	8070	0.95*
	n-Butylnitramine	0.2 *N* NaOH	2325	8460	1.00
VI	2-Nitroxyethylnitramine	0.2 *N* NaOH	2290	6320	0.79
I	Ethylenedinitramine	0.2 *N* NaOH	2360	17100	2.02
	1,7-Dinitro-1,4,7-triazaheptane	*N* KOH	2275	18600	2.18
	Propylenedinitramine-1,2	0.2 *N* NaOH	2360	17240	2.03
XIX	Methylenedinitramine	0.2 *N* NaOH	2325	17100	2.02
	1,5-Dinitro-3-nitroxy-1,5-diazapentane	0.2 *N* NaOH	2325	18400	2.16
XLIII	1,10-Dinitro-1,4,7,10-tetrazadecane-4,7-dihydrochloride	0.2 *N* NaOH	2310	16620	1.96
	1,5-Dinitro-3-methyl-3(methylenenitramine)-1,5-diazapentane	0.2 *N* NaOH	2325	28900	3.39

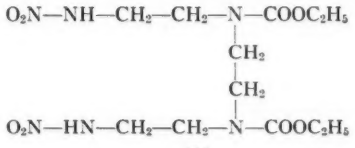
* *Data privately communicated by Dr. Carmack (see references (6), (7)).*

is changed but the alteration is relatively small. There is a significant increase in the intensity of absorption at the maximum, and the position of the maximum is shifted slightly to longer wave lengths (see Fig. 1, Curve B). The intensity at the maximum is a linear function of the number of primary nitramine groups in the molecule, and the molecular extinction constant is increased to 8500.

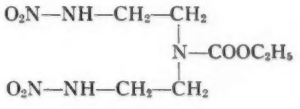
Secondary nitramines tend to be unstable in alkali, but in cases where the compounds were sufficiently stable to enable the spectra to be determined, the wave length of the maximum was unchanged from that observed in neutral solution. The intensities varied somewhat irregularly, but the variations were mostly small. In acid solution the spectra of both primary and secondary nitramines are the same as in neutral solution.

D. Distinction Between Primary and Secondary Nitramines

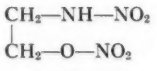
The difference in the molecular extinction constants of the primary and secondary nitramine groups suggests that such groups might be distinguished by ultraviolet spectrometry. As the difference in intensity is greater in alkaline than in neutral or acidic solution, the comparison should be made in the presence of alkali if the substance is sufficiently stable. Such characterization of the nitramine type from spectrometric data must be considered with some reserve, since in the case of three primary nitramines of known structure (IV, V, and VI) the extinction at the maximum is lower than would be calculated from the molecular extinction constant, and the intensity data actually fit better for a secondary nitramine (see also page 849).



IV



V



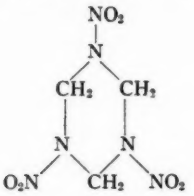
VI

E. Comments on the Spectra of Individual Compounds

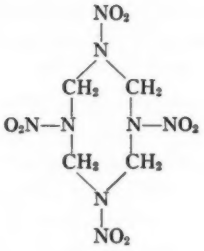
(i) 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)

The spectrum of RDX (VII) has been studied intensively in ethanol, methanol, dioxane, and water. It does not show the maximum in the neighborhood of 2300 Å, observed for most nitramines; instead there is an inflection near 2400 Å and the curve continues to rise slowly at shorter wave lengths. In water the slope in this region is slightly flatter than in methanol (Fig. 3 Curves A, B). The extinction coefficients in this flat region are lower than the values calculated for three secondary nitramine groups; this indicates

that the flattening of the curve is the result of a depression in the intensity of absorption and is not due to the superposition of additional absorption on the nitramine curve. (page 857).



VII



VIII

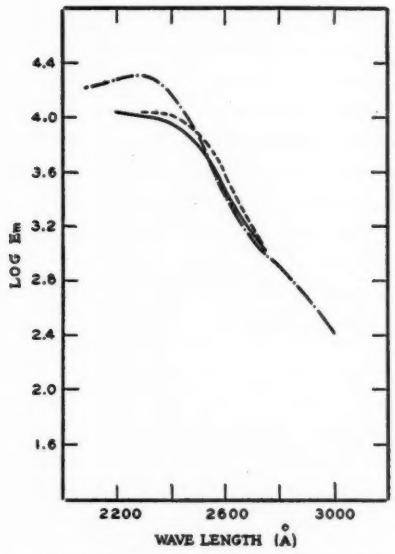
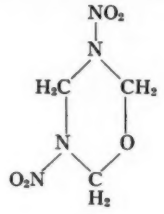


FIG. 3. *1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX).*
———— *Curve A. Solvent, methanol.*
- - - - - - - - - - - *Curve B. " water.*
1,3,5,7-Tetranitro-1,3,5,7-tetrazacycloöctane (HMX).
—·—·—·—·— *Curve C. Solvent, methanol.*

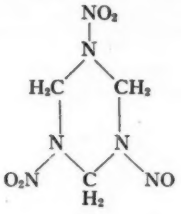
The spectrum of 1,3,5,7-tetranitro-1,3,5,7-tetrazacycloöctane (HMX) (VIII) (Fig. 3, Curve C) is normal, and the difference in shape of the curves of the two compounds is sufficient to allow the spectrographic assay of mixtures of RDX and HMX*. The spectra of RDX and HMX have also been recorded by Whitmore and Noll, whose curves agree with ours.

* *Unpublished observation from these laboratories.*

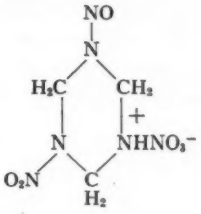
This flattening and depression of the absorption maximum has been observed also in the spectra of IX, X, XI (Fig. 13, Curves A, B). Trinitrosotrimethylenetriamine (XII) however gives a normal nitrosamine curve (page 850) and the triazacycloheptane derivative XIII gives a normal nitramine curve,



IX

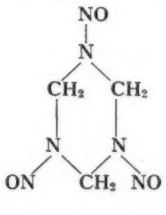


X

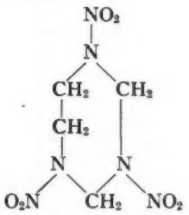


XI

though the intensity is slightly low for three nitramine groups (Fig. 13, Curve C) (E_{max} 14,900 ≡ 2.72 secondary nitramines).



XII



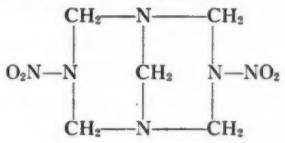
XIII

A flattening of the absorption maximum has also been observed in the spectrum of compound XLII (Fig. 18, Curve A) but in this case the effect can be reasonably attributed to the superposition of absorption from the nitrate groups on top of the nitramine absorption (see also page 859).

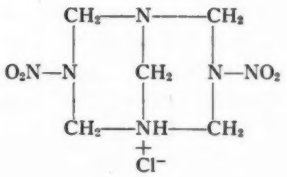
Among the primary and secondary nitramines in Tables II and III are several compounds that were obtained as intermediates or by-products in the preparation of RDX. In the case of most of these compounds the evidence of structure derived from the spectra agrees satisfactorily with the chemical data. In the case of the two compounds, XIV and XVII, some discrepancies occur and are discussed below.

(*ii*) *Dinitropentamethylenetetramine* (*DPT*)

The spectrum of DPT (XIV) is quite normal in neutral dioxane solution; there is a typical secondary



XIV



XV

nitramine maximum (Fig. 4, Curve A) at 2410 Å with an extinction coefficient of 11,000. In 0.2 *N* hydrochloric acid, however, the maximum shifts to 2150 Å (Fig. 4, Curve B) and in no other secondary nitramine has a hypsochromic shift of this kind been observed on acidification. In the accepted

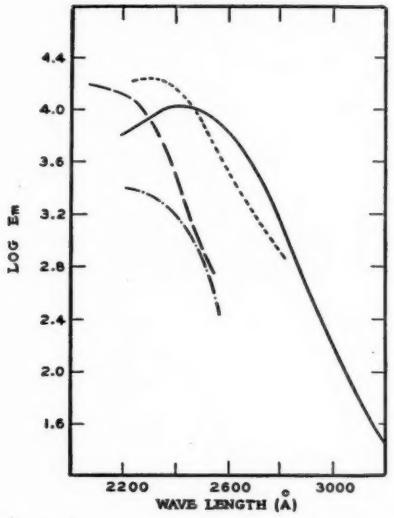
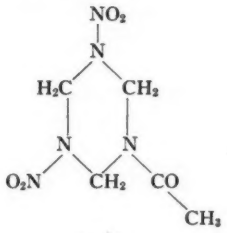


FIG. 4. *Dinitropentamethylenetetramine (DPT).*
———— *Curve A. Solvent, dioxane.*
— — — — — *Curve B. " 0.2 N hydrochloric acid.*
—·—·—·—·— *Curve C. Product from B at pH 9.*
- - - - - - - - - *Curve D. Solvent, 0.2 N sodium hydroxide.*

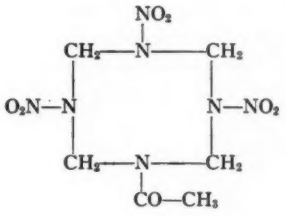
formula XIV there is a tertiary amino nitrogen atom, and the shift of the absorption maximum may be associated with the addition of a proton at this position (XV). However, as this basic nitrogen atom is separated from the nitramine chromophores by methylene groups, this explanation will hardly suffice, since the addition of a proton at this position cannot have any direct effect on the energies of the resonance states contributing to the structure of the nitramine groups. This spectrographic behavior can be reconciled with the accepted formula for DPT, if it be assumed that on the addition of dilute acid the DPT is decomposed, so that we are not dealing with a case of simple quaternary salt formation. This view receives some support from the observation that when such an acidified solution is subsequently brought to pH 9, the intensity falls off very considerably and the curve is not reproducible (Fig. 4, Curve C); the spectrum also differs considerably from that obtained when a neutral solution of DPT is made directly alkaline with 0.2 *N* sodium hydroxide (Fig. 4, Curve D).

(iii) (1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane) (TAX)

This substance was isolated by Wright and coworkers as a by-product from a Bachmann reaction carried out in the presence of a large excess of acetic anhydride (1). The analytical figures suggested a formula $C_6H_{10}O_6N_6$ or $C_5H_9O_5N_5$ and crystallographic analysis established that $C_5H_9O_5N_5$ was correct. The Franchimont test for the nitramine group was positive; analysis indicated the presence of one acetyl group, and tests for nitrate ions and nitroxy groups were negative. Wright and coworkers have proposed the structure XVI (1).



XVI



XVII

The spectrum of XVI is illustrated in Fig. 5. While this curve has the shape of a typical nitramine, the intensity at the maximum (E_m 6300 in ethanol; 6450 in dioxane) is much below that expected of a molecule containing two

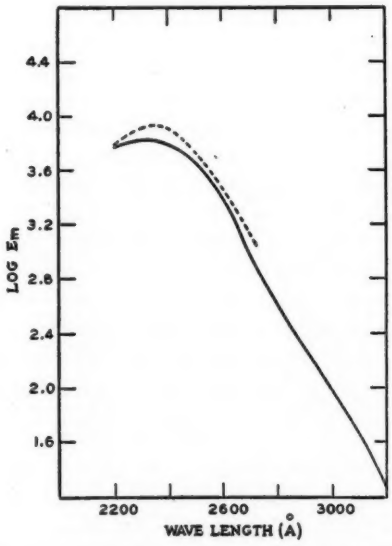
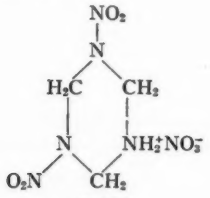


FIG. 5. *1-Acetyl-3,5-dinitro-1,3,5-triazacyclohexane.*
———— *Curve A. Solvent, ethanol.*
- - - - - - - - - *Curve B. " 0.2 N sodium hydroxide.*

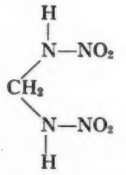
secondary nitramine groups (E_m calc. 11,000) and fits more satisfactorily for one nitramine per molecule. Compound XVII with a structure somewhat analogous to that postulated for XVI gives a normal spectrum, and the intensity of the maximum agrees with that required for three secondary nitramine groups.

F. The Spectra of Methylenedinitramine Isomers

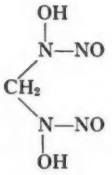
Considerable interest has been shown in the structure of two isomeric compounds of empirical formula $CH_4N_4O_4$. One of these was first prepared in 1895 by Traube by the condensation of acetone, sodium ethoxide, and nitric oxide (27) and is commonly referred to as the "Traube compound". An isomer has been obtained by J. K. N. Jones and coworkers (3) by the hydrolysis of 1,3-dinitro-1,3,5-triazacyclohexane-5-nitrate (XVIII) (PCX). It seems probable that the product of the latter reaction is the true methylenedinitramine (XIX) and the "Traube compound" is methylene-*bis*-nitrosohydroxylamine (XX).



XVIII



XIX



XX

The ultraviolet absorption spectra of these isomers have also been investigated by Carmack and Leavitt (6) and by Garwood and J. K. N. Jones (9). Determinations of the spectrum of the product from the hydrolysis of XVIII in our laboratories showed it to possess the typical curve of a primary nitramine. The maximum was at 2260 Å and the extinction coefficient was 12,530 in ethanol solution, which corresponds to 1.80 nitramine groups per molecule (Fig. 6, Curve A). In 0.2 *N* sodium hydroxide solution the maximum was shifted to 2325 Å and the extinction coefficient increased to 17,100 (2.02 nitramine groups) (Fig. 6, Curve C).

The Traube compound is unstable in the free state and is usually prepared as the mono-ammonium salt or as the disodium salt. A solution of the free acid of the Traube compound was obtained by dissolving the mono-ammonium salt in *N* hydrochloric acid. The spectrum of this solution (Fig. 7, Curve C) has a maximum at 2310 Å with extinction coefficient of 12,600; this resembles closely the curve of the hydrolysis product of XVIII and is quite acceptable as the curve of a primary nitramine. In alkaline solution, however, the absorption maximum is at 2550 Å and such a large bathochromic shift on addition of alkali has not been observed in the spectra of primary nitramines of established structure. This is illustrated in the curves of Fig. 7 and Fig. 8. While the spectrum of the free acid of the Traube compound resembles that of a primary nitramine, the spectra of its salts are clearly anomalous.

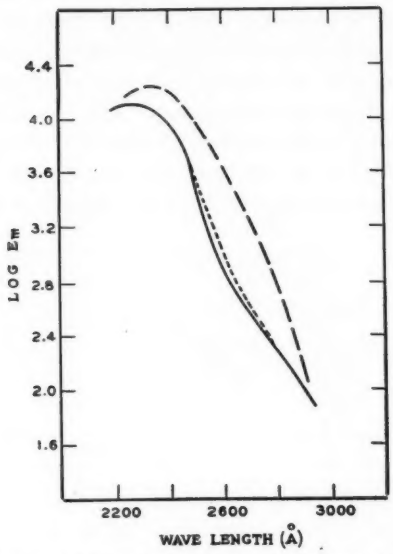


FIG. 6. *Methylenedinitramine from hydrolysis of PCX.*

———— *Curve A. Solvent, ethanol.*
– – – – – *Curve B. " 0.2 N hydrochloric acid.*
— — — — *Curve C. " 0.2 N sodium hydroxide.*

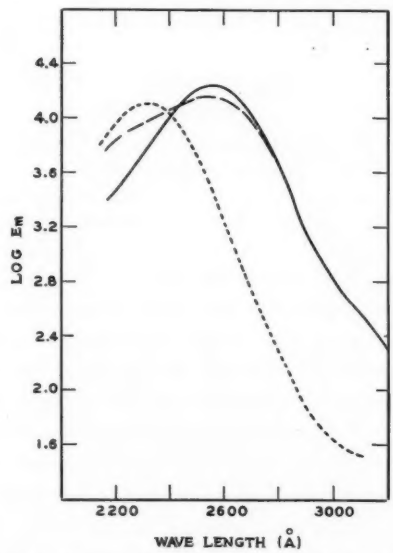


FIG. 7. *Acid ammonium salt of the "Traube compound".*

———— *Curve A. Solvent, N ammonium hydroxide.*
— — — — *" B. " water.*
– – – – – *" C. " N hydrochloric acid.*

The resemblance of the spectrum of the free acid from the Traube ammonium salt to that of the product from the hydrolysis of XVIII suggested that the Traube compound might be undergoing isomerization in acid solution, but this was disproved by the following experiment. The absorption spectrum of the disodium salt of the Traube compound was first determined in aqueous solution (Fig. 8, Curve A); the solution was then acidified with 0.2 *N* hydrochloric acid and the curve of the resulting free acid measured (Fig. 8, Curve B).

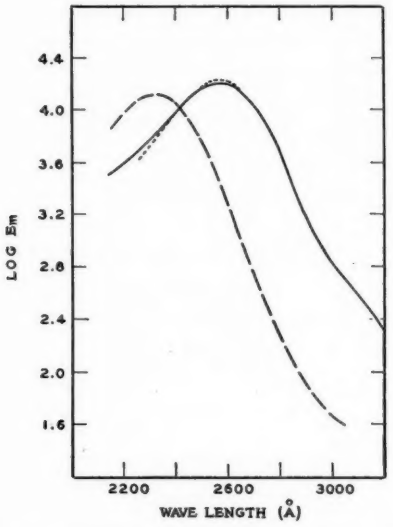


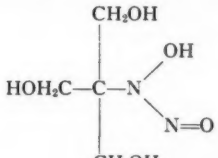
FIG. 8. *Disodium salt of the "Traube compound".*

———— *Curve A. Solvent, water.*
— — — — — " *B.* " *0.2 N hydrochloric acid.*
- - - - - - - - - " *C.* " *product from B in N potassium hydroxide.*

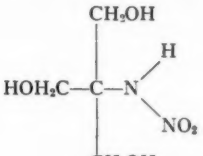
This acid solution was then made alkaline with *N* potassium hydroxide and the spectrum of the resultant salt was found to be identical with that of the original salt (Fig. 8, Curve C). These experiments showed that, although the free acid from the ammonium salt (or the disodium salt) of the Traube compound and the hydrolysis product of XVIII have similar spectra, the molecules differ in structure, since on addition of alkali the salt of the Traube compound has the maximum well displaced to longer wave lengths while that of the hydrolysis product of XVIII shows only a slight shift.

These observations have been substantiated by the results of Carmack and Leavitt (6) who have compared the spectrum of the Traube compound in neutral and in acid solution with the spectrum of a nitrosohydroxylamine derivative of established structure. The two model isomeric compounds,

N-(trimethylolmethyl)-nitrosohydroxylamine and N-(trimethylolmethyl)-nitramine (XXI, XXII), were synthesized by Cason and Prout (7) for this purpose.



XXI



XXII

The spectrum of the nitrosohydroxylamine compound (XXI) resembles that of the Traube compound very closely, both in neutral and in acid solution, and supports the formulation of the latter as (XX). The spectra of both methylenedinitramine isomers have been investigated also by Garwood and J. K. N. Jones (9), who also concluded that the product from the Traube reaction is a methylene-*bis*-nitrosohydroxylamine.

From the Traube compound it is possible to obtain two isomeric dimethyl esters. One of these (the α-methyl ester) is a white crystalline compound, with a spectrum very similar to that of the free Traube acid (Fig. 9). The β-ester is pale yellow and the spectrum shows a well developed low intensity maximum at 3800 Å. This long wave length, low intensity maximum has

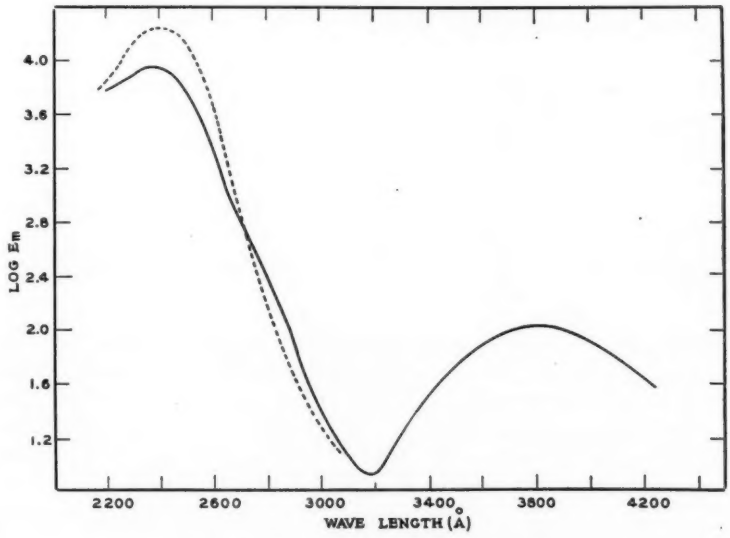
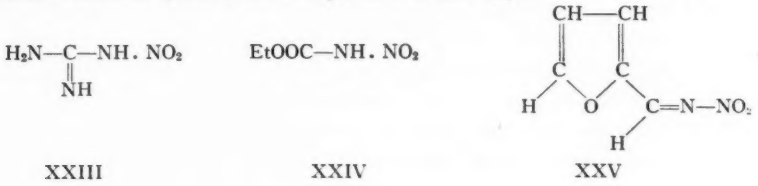


FIG. 9. *Esters of the "Traube compound".*
- - - - - - - - - - - *Curve A. α-Methyl ester (solvent, ethanol).*
———————— " *B. β-Methyl ester* (" ").

been observed in many compounds containing a nitroso group, and the structure and spectrum of this ester are discussed further on page 852. Garwood and J. K. N. Jones (9) also determined the spectra of these isomeric esters, and their curves are in good agreement with ours.

G. Nitramines Containing Conjugated Substituents

If a compound should contain a nitramine group together with a second chromophoric group so placed that a conjugated system extends from the nitramine group to the second substituent, radical changes in the spectrum would be anticipated. Nitroguanidine (XXIII), nitrourethane (XXIV), and furfural nitramide (XXV) are compounds of this type.



XXIII XXIV XXV

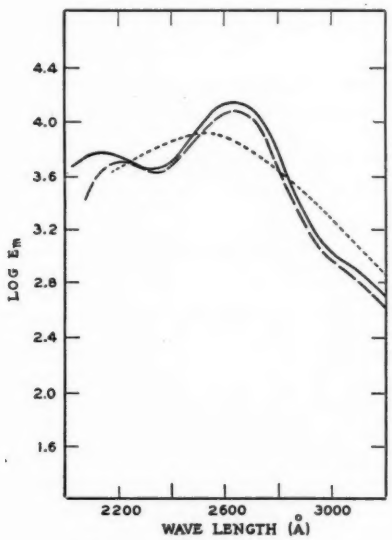


FIG. 10. *Nitroguanidine.*
——— *Curve A. Solvent, water.*
— — — — — " *B.* " *N hydrochloric acid.*
--------- " *C.* " *N sodium hydroxide.*

Nitroguanidine (Fig. 10) has a spectrum in neutral solution with two maxima; on addition of alkali this is altered and only one maximum is observed. The spectrum of nitrourethane (Fig. 11) possesses, in neutral solution, a single maximum of high intensity (Curve C); in 0.2 *N* sodium hydroxide two maxima

appear (2600 and 2100 Å) and the spectrum closely resembles that of the potassium salt in water (Curve A); in 0.2 *N* hydrochloric acid the spectrum

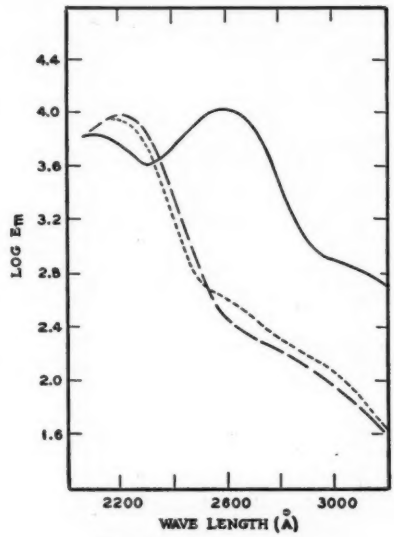
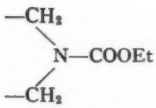


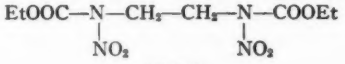
FIG. 11. *Nitrourethane.*
——————— *Curve A. Potassium salt in water.*
— — — — — " *B. Solvent, 0.2 N hydrochloric acid.*
- - - - - - - - - " *C. " ethanol.*

is the same as in water. The spectrum of nitrourethane in alkaline solutions bears a close resemblance to that of a neutral solution of nitroguanidine. Ethanol solutions of furfural nitramide (Fig. 12) show maxima at 3200 and 2700 Å.

H. Compounds Containing Carboethoxy Groups

Two compounds (IV, V) containing the grouping  as well as primary nitramine groups are recorded in Table III. In these the carboethoxy substituents are not conjugated with the nitramine groups; the shapes of the curves are similar to that of simple nitramines, but the intensities are appreciably low. The calculated values for the absorption maxima of both IV and V based on the molecular extinction constant is 14,000, while the observed values are 11,500 and 11,200 respectively.

Compound XXVI contains two carboethoxy groups substituted



XXVI

directly into the nitramine chromophore. The spectrum is of the typical nitramine type, but in this case also the intensity is slightly low (see Table II). This compound should be compared with nitrourethane (Fig. 11).

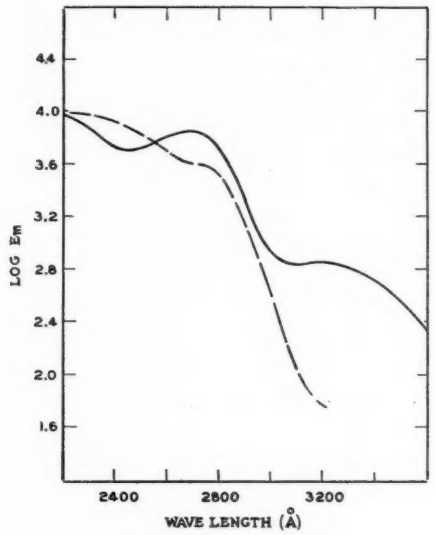
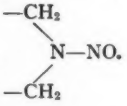


FIG. 12. *Furfural nitramide.*
———— *Curve A. Solvent, ethanol.*
— — — — — " *B.* " *0.2 N sodium hydroxide.*

III. The Spectra of Nitroso Compounds

A. Nitrosamines

The number of nitrosamines included in these studies has been relatively small; they are all of the secondary type, containing the grouping 

These compounds contain either a nitrosamine group alone, or a nitrosamine group together with a nitramine group. They show two absorption maxima, one in the same region as the nitramine maximum and of the same order of intensity, another at 3600 to 3850 Å with a molecular extinction coefficient of the order of 100. This low intensity maximum may show evidence of fine structure resolution. It is the end absorption of this band that imparts a pale yellow color to many nitrosamines. The intensities of absorption at the maxima appear to vary appreciably from one nitrosamine to another, and with the rather limited data available it does not seem possible to establish any simple relations between the number of nitramine and nitrosamine groups

in the molecule and the intensities at the maxima. These spectra are summarized in Table VII. Typical examples are illustrated in Fig. 13, Curves B, C, and D.

TABLE VII

ABSORPTION SPECTRA OF SECONDARY NITROSAMINES
POSITIONS AND INTENSITIES OF THE MAXIMA

Structure	Compound	Solvent	Absorption maxima			
			λ_{max}	E_{max}	λ_{max}	E_{max}
X	1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane	Ethanol	*		3650	48
	N-Nitro-N′-nitrosopiperazine	Ethanol	2420	12900	3600	123
XI	1-Nitroso-3-nitro-1,3,5-triazacyclohexane-5-nitrate	Ethanol Benzene	*		3740 3850	69 66.3
	1-Nitroso-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane	Acetone Ethanol	2280	18750	3760	69
	Dinitrosopentamethylenetetramine	Ethanol	2300	10740	3675	115
XII	1,3,5-Trinitroso-1,3,5-triazacyclohexane	Ethanol	2350	13200	3700 3820	174 166

* *These compounds show a plateau only in this region* (*see page 841*).

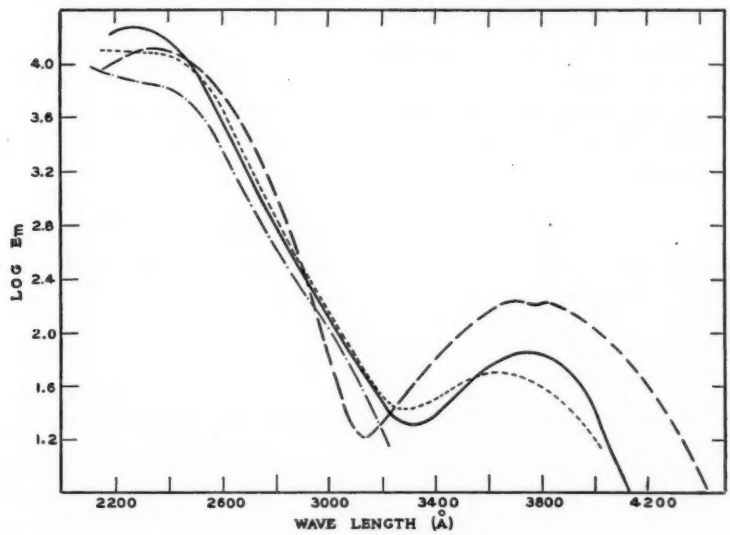
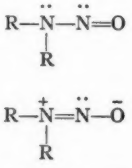


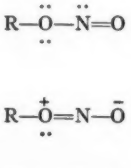
FIG. 13.

Curve A. 1-Oxa-3,5-dinitro-3,5-diazacyclohexane.
" B. 1,3-Dinitro-5-nitroso-1,3,5-triazacyclohexane.
" C. 1,3,5-Trinitroso-1,3,5-triazacyclohexane.
" D. 1-Nitroso-3,5,7-trinitro-1,3,5,7-tetrazacycloöctane.
Solvent, ethanol.

The absorption maximum at 3600 to 3850 Å in the nitrosamine spectrum resembles similar structure in the spectra of the alkyl nitroso compounds such as amyl nitrite (2, 5, 9), and octyl nitrite (23). In both types of compounds the resonating structures which probably predominate show some similarity (XXVII - XXVIII).



XXVII Nitrosamine resonance

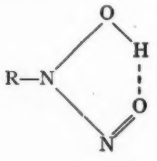


XXVIII Nitrosoalkane resonance

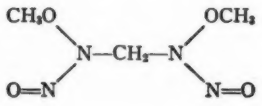
B. Nitrosohydroxylamines

When the close similarity of the spectrum of the "Traube compound" to that of a typical nitramine was first observed (see page 847), the absence of a long wave "nitroso band" was considered fairly conclusive evidence *against* the formulation of that compound as a nitrosohydroxylamine derivative (XX). Later, Carmack, and Leavitt (6) reported the absorption spectrum of a nitrosohydroxylamine (XXI) synthesized by Cason by an unequivocal method and it was noted that the long wave "nitroso band" was absent from the spectrum of this compound also.

The disappearance of the "nitroso band" in these hydroxy derivatives may be the result of hydrogen bonding as shown in XXIX. The β-methyl ester of the Traube compound, which has a typical nitrosamine spectrum, may be represented by XXX, in which the hydrogen bonding has been destroyed by the introduction of the methyl group.



XXIX



XXX

IV. The Spectra of Nitroxy Groups and Nitrate Ions

The nitrate ion (NO_3^-) and the nitroxy group (—O—NO_2) give rise to quite different spectra. The nitrate ion spectrum has a very low intensity maximum near 3000 Å (19), and the absorption rises very steeply in the further ultraviolet region (Fig. 14, Curve B). The nitroxy group gives a spectrum in which there is no maximum, but a sharp inflection occurs near 2600 Å (Fig. 14, Curve A). The spectrographic data for compounds containing ionized nitrate groups which we have examined are summarized in Table VIII, and the data for the nitroxy inflection are listed in Table IX. For the ionized nitrate

group a molecular extinction constant of 7.6 at the maximum has been assigned. For the nitroxy inflection the assignment of a similar constant to the intensity at the point of inflection is hardly justified on the basis of the

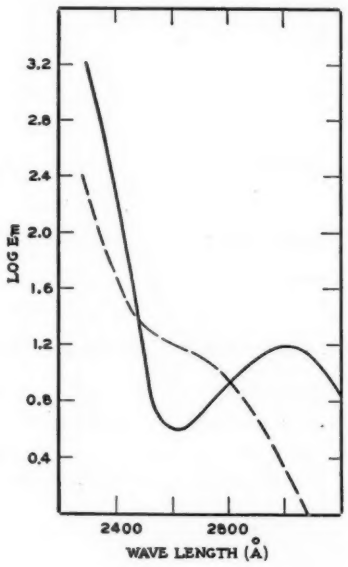


FIG. 14.

— — — — — *Curve A. Nitroxyethane (solvent, ethanol).*
———— " *B. Ethylenediamine dinitrate (solvent, water).*

TABLE VIII

ABSORPTION SPECTRA OF COMPOUNDS CONTAINING NITRATE IONS
POSITION AND INTENSITY OF THE MAXIMUM

Compound	Solvent	Absorption max.		$E_{max}/7.6$
		λ, Å	E_{max}	
Ammonium nitrate	Water	3015	7.6	1.00
Hexamine mononitrate	Water	3015	9.1	1.20
Hexamine-(N-acetylaminomethyl)-nitrate	Water	3015	7.8	1.05
Ethylenediamine dinitrate	Water	3015	15.0	1.95
Hexamine dinitrate	Water	3015	18.6	2.35

data at present available; however, for the purpose of the calculations described in the following paragraph we have assumed the value of 14.8 at 2650 Å, taken from the curve for nitroxyethane.

TABLE IX

ABSORPTION SPECTRA OF COMPOUNDS CONTAINING NITROXY GROUPS
POSITION AND INTENSITY OF THE POINT OF INFLECTION

Compound	Solvent	Absorption at point of inflection	
		λ, Å	E_{molar}
Nitroxyethane	Ethanol	2650	14.8
2,3,4-Triacetyl-α-methyl-D-glucoside-6-nitrate	Methanol	2650	20.2
α-Methyl-D-glucose-6-nitrate	Water	2650	19.0
2,3,4-Trimethyl-β-methyl-D-glucose-6-nitrate	Ethanol	2650	21.4
3,4,6-Triacetyl-β-methyl-D-glucose-2-nitrate	Methanol	2700	26.2

V. Spectra of Compounds Containing Mixed Groups

A. Nitroxy Groups and Nitrate Ions

In Figs. 15 and 16 are illustrated the spectra of four compounds that contain both nitrate ions and nitroxy groups. The shape of these curves is quite characteristic, and the question arises whether the number of each type

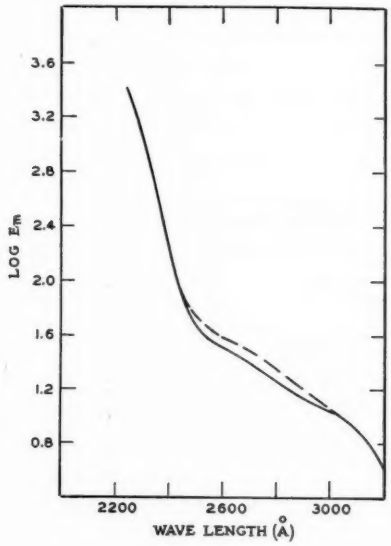


FIG. 15.

———— *Curve A. 1,5-Dinitroxy-3-azapentane nitrate (XXXIII).*
— — — — " *B. 2,6-Dinitroxy-4-azaheptane nitrate (XXXII).*
(Solvent, water).

of group in the molecule can be deduced from the appearance of the absorption curve. Comparison of the spectra of nitroxyethane (Fig. 14, Curve A) and ethylenediamine dinitrate (XXXI) (Fig. 14, Curve B) shows that the

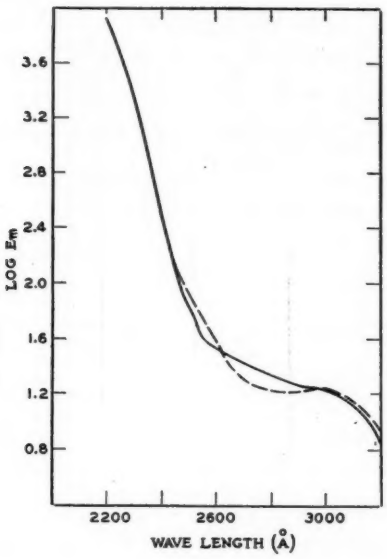


FIG. 16.

———— *Curve A. 1,8-Dinitroxy-3,6-diazaoctane dinitrate (XXXIV).*
— — — — — " *B. 1-Nitroxy-3,6-diazahexane dinitrate (XXXV).*
(Solvent, water).

minimum in the nitrate ion curve occurs in the same region as the inflection in the spectra of nitroxy compounds. In compounds containing both groups, but no other chromophoric centers, the shape of the curve should vary considerably with the ratio

$$\frac{\text{Number of nitroxy groups}}{\text{Number of nitrate ions}}$$

in the molecule. The over-all intensity should also vary with the total number of groups present, so that it should be possible from an analysis of the shape and position of the absorption curve to determine the actual number of each type of group present.

$$NO_3^- \quad NH_3^+—CH_2—CH_2—NH_3^+ \quad NO_3^-$$

XXXI

As yet, insufficient data on compounds containing both types of groups are available to establish this with any certainty. In Table X we have

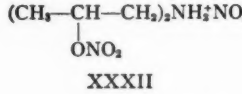
calculated the ratios of the extinction coefficients; $\frac{E_{2650}}{E_{3020}}$ for the four compounds XXXII to XXXV, and compared these with the ratios calculated on the basis of molecular extinction constants of 7.6 at 3020 Å and 1.9 at 2650 Å for the

TABLE X

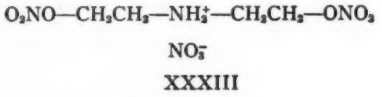
ANALYSIS OF SPECTRA OF COMPOUNDS CONTAINING BOTH NITRATE IONS AND NITROXY GROUPS

Compound	Ratio $\frac{(-O-NO_2)}{(NO_3)}$	Extinction coefficient predicted from molecular extinction constants			Extinction coefficient observed		
		E_{2650}	E_{3020}	$\frac{E_{2650}}{E_{3020}}$	E_{2650}	E_{3020}	$\frac{E_{2650}}{E_{3020}}$
XXXII	$\frac{2}{1}$	31.5	11.4	2.76	34.6	10.5	3.29
XXXIII	$\frac{2}{1}$	31.5	11.4	2.76	28.2	9.6	2.94
XXXIV	$\frac{2}{2}$	33.4	19.0	1.75	30.2	17.4	1.73
XXXV	$\frac{1}{2}$	18.6	17.1	1.08	25.0	17.8	1.40

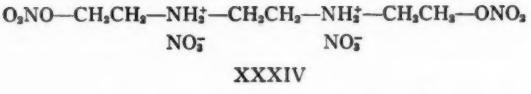
nitrate ion group, and 1.9 at 3030 Å and 14.8 at 2650 Å for the nitroxy group. The calculated values for the ratio E_{2650}/E_{3020} vary from 1.08 for an ester/ion ratio of 1/2, to 2.76 for an ester/ion ratio of 2/1.



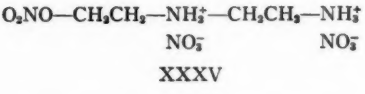
XXXII



XXXIII



XXXIV



XXXV

These results give promise that a spectrographic method for the simultaneous determination of the number of nitroxy and nitrate ion groups in a molecule may be developed, but the method must be tested on more compounds of known structure.

B. Nitramine and Nitroxy Groups

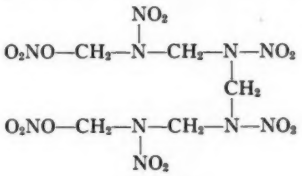
In compounds containing both nitramine and nitroxy groups, the nitroxy inflection at 2650 Å does not produce any apparent change in the shape of the absorption curve. This is true even when the molecule contains two

nitroxy groups and only one nitramine group (XL). In compound XXXVI there is a slight inflection at 2750 Å (Fig. 17, Curve B), but a similar inflection is present also in the spectra of other nitramine compounds that do not contain nitroxy groups, e.g., XLI (Fig. 17, Curve A).

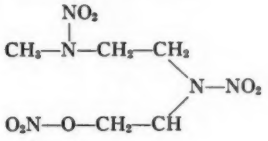
It is probable that the nitroxy group does have a secondary effect on the intensity of the nitramine maximum, as the nitroxy chromophore produces rapidly increasing absorption in this region of the spectrum. In Table XI the spectra of five compounds (XXXVI – XL) containing both secondary nitramine and nitroxy groups are arranged in increasing order of the ratio

$$\frac{\text{Number of nitroxy groups}}{\text{Number of nitramine groups}}$$

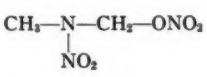
Except for the compound in which this ratio is 0.5, the observed



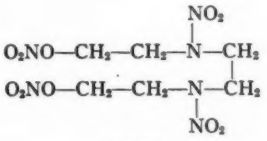
XXXVI



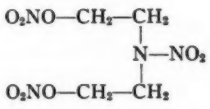
XXXVII



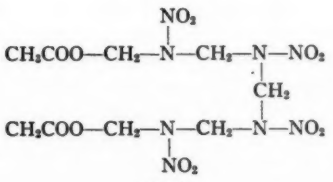
XXXVIII



XXIX



XL



XLI

intensity of the nitramine maximum is higher than that calculated from the molecular extinction constant, and this discrepancy increases with increase in the above ratio.*

C. Nitrate Ions and Nitramine Groups

The absorption maximum at 3015 Å associated with the nitrate ion is of such low intensity that it is completely "swamped" by the end absorption of

* *Note however that in 2-nitroxyethylnitramine, which contains one nitroxy and one primary nitramine group, the intensity observed for the primary nitramine maximum is sensibly diminished (Table III).*

the nitramine band, e.g., in the spectrum of XVIII there is no sign of nitrate ion absorption. At short wave lengths, however, the nitrate ion curve rises very steeply, and it may be significant that the spectrum of compound XLII

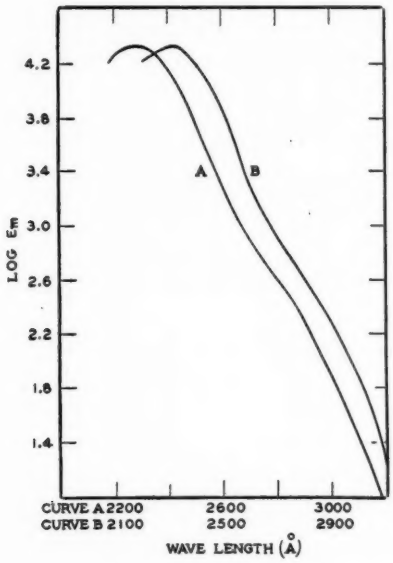


FIG. 17.

Curve A. 1,9-Diacetoxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (XLI).
" B. 1,9-Dinitroxy-2,4,6,8-tetranitro-2,4,6,8-tetrazanonane (XXXVI).
(Solvent, dioxane).

TABLE XI

EFFECT OF NITROXY GROUP ON THE INTENSITY OF THE SECONDARY NITRAMINE MAXIMUM

Compound	Ratio $\frac{\text{Nitroxy groups}}{\text{Nitramine groups}}$	E_{max}		$\frac{E_{max.}\text{ obs.}}{E_{max.}\text{ calc.}}$
		Calc.	Observed	
XXXVI	$\frac{2}{4}$	22,000	21,900	1.00
XXXVII	$\frac{1}{2}$	11,000	11,850	1.07
XXXVIII	$\frac{1}{1}$	5,500	6,700	1.23
XXXIX	$\frac{2}{2}$	11,000	12,000	1.10
XL	$\frac{2}{1}$	5,500	7,350	1.34

shows an inflection in the curve instead of a maximum (Fig. 18, Curve A), whereas with the corresponding chloride XLIII the ordinary nitramine maximum is observed (Fig. 18, Curve B.).

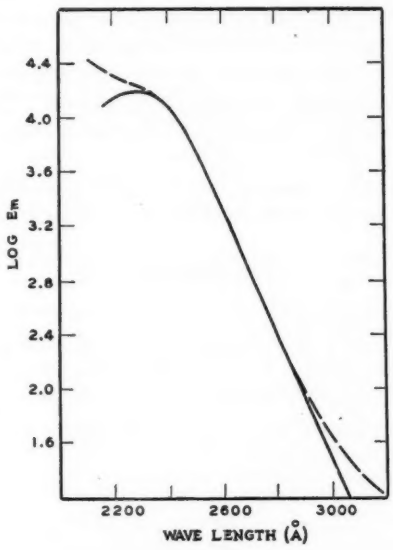


FIG. 18.

— — — — — *Curve A. 1,10-Dinitro-1,4,7,10-tetrazadecane dinitrate (XLII).*
———— " *B. 1,10-Dinitro-1,4,7,10-tetrazadecane dihydrochloride (XLIII).*
(Solvent, water).

$$O_2N{-}NH{-}CH_2{-}CH_2{-}\underset{NO_3^-}{NH_2^+}{-}CH_2{-}CH_2{-}\underset{NO_3^-}{NH_2^+}{-}CH_2{-}CH_2{-}NH{-}NO_2$$

XLII

$$O_2N{-}NH{-}CH_2{-}CH_2{-}\underset{Cl^-}{NH_2^+}{-}CH_2{-}\underset{Cl^-}{NH_2^+}{-}CH_2{-}CH_2{-}NH{-}NO_2$$

XLIII

VI. Experimental

The spectra were measured on a Beckman model D.U. ultraviolet spectrometer; a slit width of 20 Å was employed between 2100 and 2350 Å and of 10 Å at longer wave lengths. The compounds were analytically pure samples. In no case was any evidence of reaction with the solvent or photochemical change observed.

VII. Concluding Remarks

The compounds included in this survey were selected mainly on the basis of their ready availability and because of their bearing on the elucidation of

the structure of compounds of specific interest in connection with the chemistry of RDX. Certain qualitative and quantitative relations between the chemical structure and the absorption spectra were observed. These results suffice to indicate that a more comprehensive survey of the ultraviolet absorption spectra of nonaromatic nitrogen containing compounds would probably lead to the establishment of additional correlations which could be of considerable help in the determination of the structure of nitrogenous compounds, including compounds from biological sources. Such a survey might profitably include the alkyl nitrites and the nitrite salts of organic acids as well as C-nitro and C-nitroso compounds.

The infrared absorption spectra between 4000 and 850 cm.$^{-1}$ of many of the compounds discussed here have been determined also and will be described in a later publication.

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SOME PROPERTIES OF CESIUM–AMMONIA SOLUTIONS[1]

By J. W. Hodgins

Abstract

Measurements of vapor pressure, liquid density, and electrical conductance were made on solutions of cesium in liquid ammonia. The solutions differ from those of the other alkali metals in that there is no indication of liquid–liquid phase separation for concentrations 0.04 *N* to 7 *N*. Experiments on rings of solution frozen in liquid nitrogen make it appear unlikely that the system is superconducting at 77° K.

Introduction

Considerable investigation has been carried out recently (1-3, 6, 7, 9, 10, 16-22) on the characteristics of solutions of alkali metals and alkaline earth elements in liquid ammonia, with particular regard to their electrical conductance at low temperature. Much of the renewed interest in these solutions was occasioned by the report of R. A. Ogg, Jr. (20) on the persistence of currents induced in rings of frozen solutions of sodium in liquid ammonia. This phenomenon was regarded as evidence of superconductivity in the frozen solution at temperatures up to about 180° K., a very high temperature compared to the transition temperature heretofore observed for any metal or alloy.

The only experiments confirming the observation of these persistent currents were reported by the author in 1946 (10), although the technique of these experiments differed from that of Dr. Ogg. Also the strength of the current produced was less and of shorter duration, and the observations were all made at 90° K. Further comment will be made on these experiments in a later note.

Since the persistent currents observed with frozen sodium solutions were so feeble and so short-lived, and particularly since their appearance was so sporadic, it was decided, on taking up the study again, to examine the frozen solutions of other alkali metals for the persistence of an induced current. Lithium had already yielded negative results, and cesium was chosen for the study, its low ionization potential being an additional reason for its choice. Since the only positive answers with the sodium solution were obtained when the concentration of the solution was in the region of liquid–liquid phase separation (upper consolute temperature = −41.5° C. at a mole ratio $NH_3 : Na = 25 : 1$), it was first necessary to establish the concentration region within which liquid–liquid phase separation occurs for the cesium–ammonia solution. It was also found desirable to know the solubility of the metal in ammonia, the vapor pressure of the solutions, the density of the solutions, and the electrical conductance.

[1] *Manuscript received July 22, 1949.*

Contribution from the Defence Research Chemical Laboratories, Ottawa, Canada. Issued as DRCL No. 30.

Experimental

(A) Apparatus

1. Determination of Vapor Pressure of Cesium–ammonia Solutions

An isothermal curve of vapor pressure as a function of concentration was required for three reasons. First, in subsequent experiments, it gave a convenient method of determining the concentration. Second, the curve would indicate, by a flat portion parallel to the concentration axis the region where two liquid phases were present. Third, the lower portion of the curve will become parallel to the concentration axis when the ammonia is saturated with cesium; this gives the solubility.

Since cesium is relatively rare, early attempts were made to combine the measurements of vapor pressure with those of conductance, but manipulative considerations indicated that these determinations would be better carried out separately. The plan for the vapor pressure measurements was to start with the strongest solution to be dealt with, and progressively dilute it with ammonia, a vapor pressure determination being made after each dilution.

Anhydrous ammonia (Matheson Alkali Company, East Rutherford, N.J.) was poured under pressure into a smaller cylinder to which had been added about 50 gm. of freshly cut sodium. This small cylinder was of the type designed by Kraus, and indeed was procured from Brown University. The sodium ensured the absolute dryness of the ammonia, and, after all the hydrogen had been blown off, the ammonia was added directly to the vacuum system from the cylinder. A sintered glass disk (*H*, Fig. 1) was inserted in the line to filter out any particles of sodamide that might be carried in the ammonia stream.

Metallic cesium (A. D. McKay Co., New York) was distilled in a weighed apparatus and sealed into frangible glass ampoules, to be broken *in vacuo* by a magnetic hammer as required.

The vapor pressure apparatus is illustrated in Fig. 1. *A* is a pressure release that allows ammonia to escape when its pressure exceeds a predetermined value. The escaped ammonia is absorbed in the water above the mercury in the blowoff. *C* is a calibrated volume (5440 ml.), *D* is the cell in which the cesium solution was prepared, and *E* a glass plunger activated by the solenoid *F* (a piece of iron is sealed into the shaft of *E*). The plunger is suspended on a steel spring, and is used as a stirrer by the application of an intermittent current to the solenoid, using an electronic interrupter as the source. The temperature of the solution in the tube is obtained by means of a calibrated thermocouple (*T.C.*) in a well dipping into the solution. Potentials were read on a Rubicon High Precision potentiometer, with a sensitivity of 0.5 μv. Vapor pressures were read on manometer *G*, furnished with a mirror scale. All the volume elements of the apparatus were calibrated before use, and corrections were applied to the solution concentrations wherever the volume of vapor in the lines became significant.

All the vapor pressure measurements were performed at −50° C., a temperature judged to be high enough to permit sufficiently large pressure readings, and possibly low enough to be below the consolute temperature for liquid–liquid phase separation, when the vapor pressure would be independent of

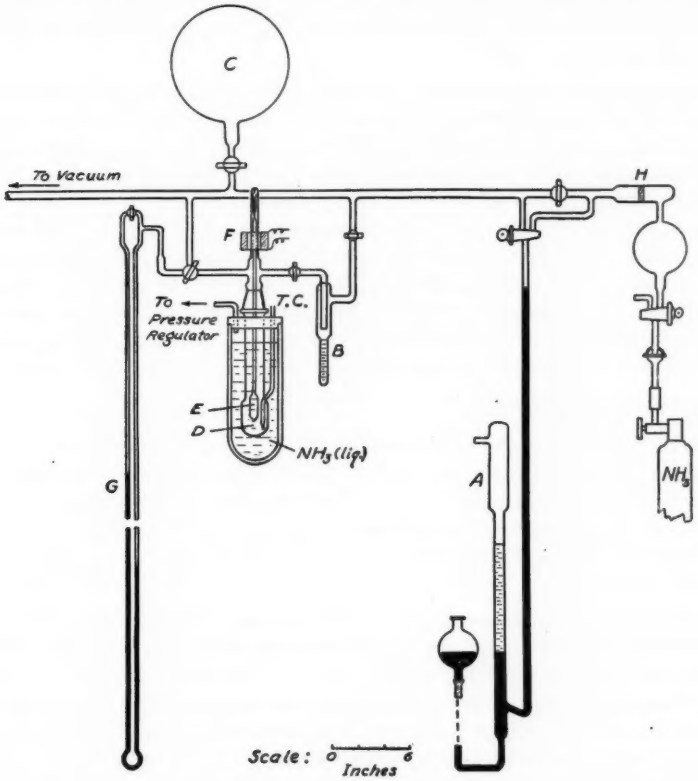

FIG. 1. *Apparatus for measuring vapor pressures.*

over-all concentration. The temperature of −50° C. was maintained by boiling liquid ammonia under reduced pressure in a Dewar flask around the vapor pressure tube. The Dewar flask was sealed to the rubber collar around the vapor pressure tube with plasticine (since it had to be removed frequently) and the pressure above the liquid ammonia reduced by means of a glass aspirator pump. When the vapor pressure was reached corresponding to −50° C. (311 mm.) a regulator took over and maintained the pressure constant. This manostat made it possible to hold any temperature between −35° C. and −70° C. constant to ± 0.02° C.

For the determination reported here, three ampoules containing a total of 3.825 gm. of pure cesium were put into tube *D*, which was evacuated. The

ampoules were broken by the magnetically operated plunger *E*. The required quantity of ammonia, previously measured in trap *B* and a calibrated bulb, was condensed into tube *D*, which was refrigerated in liquid air. The flask of liquid air around *D* was replaced by a flask of liquid ammonia, a seal was made with the rubber collar, and the manostat put into operation. The solution was stirred, and vapor pressure readings were made when the temperature was steady at −50° C.

This procedure was repeated for each point on the vapor-pressure curve by adding the appropriate quantity of ammonia necessary to attain the dilution desired. After vapor pressures had been recorded for 12 concentrations, all the ammonia was distilled from the cesium and the total quantity of ammonia added in one operation to give a concentration corresponding to the thirteenth point on the curve. No discontinuity was observed in the curve and thus the results were regarded as valid. As a final check on concentration the cesium was converted at the conclusion of the experiment to the ethoxide, water was added, and the hydroxide solution evaporated to dryness to expel remaining traces of ammonia. Determination of the cesium by titration with standard acid resulted in excellent agreement with the original quantity of cesium used.

2. Measurements of Density

Sodium solutions in liquid ammonia show a rather large increase in specific volume (14). That is, the total volume of solution is considerably higher than the sum of the volumes of its two constituents. Accordingly, it was of interest to determine whether the same expansion is characteristic of cesium solutions, and this determination was accomplished by measurements of the solution densities.

The densities were measured at −50° C., using a Westphal balance in an apparatus similar to that used by Kraus, Carney, and Johnson (14). A diagram of the apparatus is given in Fig. 2. The float (volume = 2.62 ml. at −50° C.) was suspended in the solution by means of a platinum wire (No. 38 B.S.S.). When it was necessary to evacuate the tube a closure was obtained by squeezing a piece of gum rubber tube around the wire by means of a pinchclamp—a device that gives a surprisingly tight seal.

A solution of known concentration was produced in the bottom of the tube by adding a weighed quantity of cesium *in vacuo* and distilling in the appropriate quantity of ammonia. With the solution held at −50° C. by the boiling ammonia cryostat, the solution was stirred by introducing a few bubbles of hydrogen through tube *A*, the hydrogen being added until the tube had reached atmospheric pressure. During the actual weighing of the float it was, of course, necessary to exclude air from the solution. Accordingly, when the pinchclamp closure around the wire at the top of the tube was opened, a brisk flow (100 ml. per min.) of hydrogen–ammonia was started through *B* and *C* (Fig. 2) to maintain a positive pressure at the mouth of the tube. The flow rates of hydrogen and ammonia were so regulated that the partial pressure of ammonia in the gas mixture corresponded to the vapor

pressure of ammonia over the solution being investigated. Thus, loss of ammonia vapor to the gas stream during the weighings was avoided. At the conclusion of the experiment the total quantity of ammonia and the weight of cesium present were checked by analysis and found to be as expected.

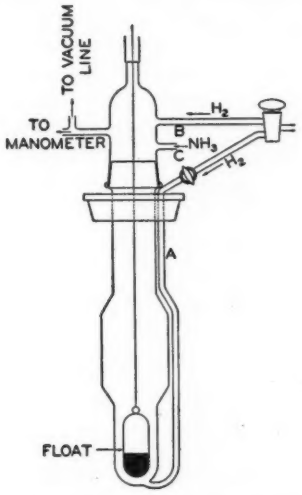

FIG. 2. *Apparatus for measuring solution densities.*

3. *Electrical Conductivity*

The electrical conductance of the cesium–ammonia solutions was required for comparison with the conductance data reported for sodium and potassium solutions by Kraus and Lucasse (13, 15). Also, a careful study of conductance should reveal the presence of any liquid–liquid phase separation under the conditions employed, and it was of interest to observe the change of conductance on freezing. Several types of cell were tried for these measurements, and the final design was adopted only after several facts were appreciated:

(1) The conductance of these solutions is, like that of the other alkali metal solutions in ammonia, very high. Accordingly, the cell must be designed to give a long current path and a small conductor cross section.

(2) The reaction of cesium with ammonia is much more rapid than that of the other alkali metals, and it is catalyzed by the presence of cesium amide. This fact precluded the use of a capillary cell and necessitated geometry that would allow bubbles of hydrogen to rise out of the current path.

(3) The cell geometry had to allow for adequate mixing of the solution after each addition of ammonia, since the cost of cesium and the manipulative difficulties made it preferable to start with a concentrated solution and dilute it several times before renewal.

(4) It was necessary to have a constant cross section for the current path.

(5) The cell had to remain vacuum-tight even after freezing in liquid air and remelting. This requirement was perhaps the most difficult to fulfill.

The conductance cell is shown in Fig. 3. The tube in which the platinum electrodes are located has a capacity of about 2 ml. Since platinum sealed

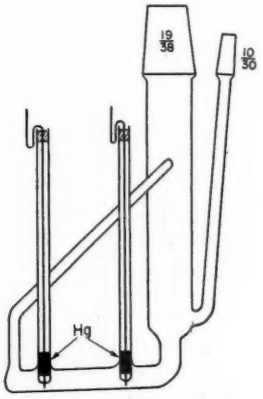

FIG. 3. *Conductance cell.*

through Pyrex is not vacuum-tight, mercury is used in the electrode wells. This ensured the tightness of the apparatus even when the mercury was frozen. The tube leading from the end of the electrode chamber diagonally back to the vertical tube is for stirring the solution. For this experiment, cesium metal was sealed into tubes 3 mm. in diameter. An appropriate length of one of these tubes was broken off, and introduced in the side arm on the cell. When melted *in vacuo*, the cesium ran down into the body of the cell. When fresh ammonia had been distilled into the cell, the frozen solution was melted and the cell tilted clockwise (with reference to Fig. 3); this provided adequate mixing.

The electrodes were lightly platinized and the cell constant was determined with standard potassium chloride solutions at 25° C., using Shedlovsky's figures (23). Two bridges were used for the measurement of resistance. For the dilute solutions (up to a concentration of $NH_3 : Cs = 20 : 1$), a conventional type of a-c. conductance bridge was employed, using a 1000 cycle oscillator as the source, with a Leeds and Northrup Kohlrausch slidewire for the ratio arms, and a DuMont oscilloscope as the balance detector.

The conductance of the more concentrated solutions is very high and is electronic rather than electrolytic, as demonstrated so clearly by Kraus and others (12, 15). Thus, in the range where the a-c. conductance measurements were becoming more difficult owing to capacity effects, a Leeds and Northrup

direct-current bridge having a sensitivity of better than 0.001 ohm was employed. As the current direction was reversed on each successive measurement, there was little to fear from polarization interference. A range of concentrations from 0.05 N to 6.7 N was studied at $-70 \pm 0.2°$ C. Conductance measurements were made too on the solutions when frozen in liquid air. The temperature of $-70°$ C. was chosen as the experimental temperature because it was felt that a check on the possible formation of two liquid phases could thus be obtained. That is, since the electrodes are at the bottom of the cell, and if two liquid phases did form, the conductance of the tranquil solution would be different from that of the agitated solution when the two phases were intermixed. Accordingly, measurements of conductance were made at each concentration of the solution immediately after violent agitation and also after long standing. No difference in conductance was observed at any time.

To maintain the conductance cell at $-70°$ C., it was immersed in stirred acetone contained in a nickel beaker surrounded by "dry-ice "snow. A thermoregulator operated a heater that maintained the bath at the required temperature.

(B) Experimental Results

1. Vapor Pressure of Cesium Solutions at $-50°$ C.

The vapor pressure curve in Fig. 4 is drawn from the following data:

Wt. of cesium used = 3.825 gm. = 0.0287 gm-atoms of cesium.

TABLE I

Solution No.	Moles NH_3	Mole ration NH_3 : Cs	V.p., mm. Hg
1	0.0505	1.76	43.5
2	0.0636	2.22	43.8
3	0.0736	2.57	44.9
4	0.0832	2.90	46.3
5	0.0891	3.11	47.6
6	0.0951	3.31	51.0
7	0.1011	3.52	56.2
8	0.1071	3.73	59.0
9	0.1130	3.94	63.8
10	0.1190	4.15	72.7
11	0.1249	4.36	80.0
12	0.1296	4.52	83.3
13	0.1309	4.56	84.9
14	0.1396	4.87	97.4
15	0.1497	5.22	113.1
16	0.1598	5.54	128.6
17	0.1699	5.92	146.9
18	0.1905	6.57	177.0
19	0.2110	7.34	203.4
20	0.2316	8.07	224.6
21	0.2653	9.24	245.7
22	0.2805	9.79	252.6
23	0.2957	10.30	257.2
24	0.2931	10.21	258.0

TABLE I—*Concluded*

Solution No.	Moles NH_3	Mole ration NH_3 : Cs	V.p., mm. Hg
25	0.3032	10.56	260.0
26	0.3109	10.83	264.7
27	0.3260	11.35	268.3
28	0.3412	11.90	273.5
29	0.3564	12.41	277.0
30	0.3716	12.95	284.6
31	0.4026	14.02	282.8
32	0.4026	14.02	284.0
33	0.4177	14.55	285.8
34	0.4328	15.09	286.8
35	0.5035	17.54	291.8

The dotted curve in Fig. 4 is that of vapor pressure as a function of concentration, if the solution obeys Raoult's law. Pure ammonia has a vapor pressure at −50° C. of 310.7 mm. (5). The last point shown on the curve in

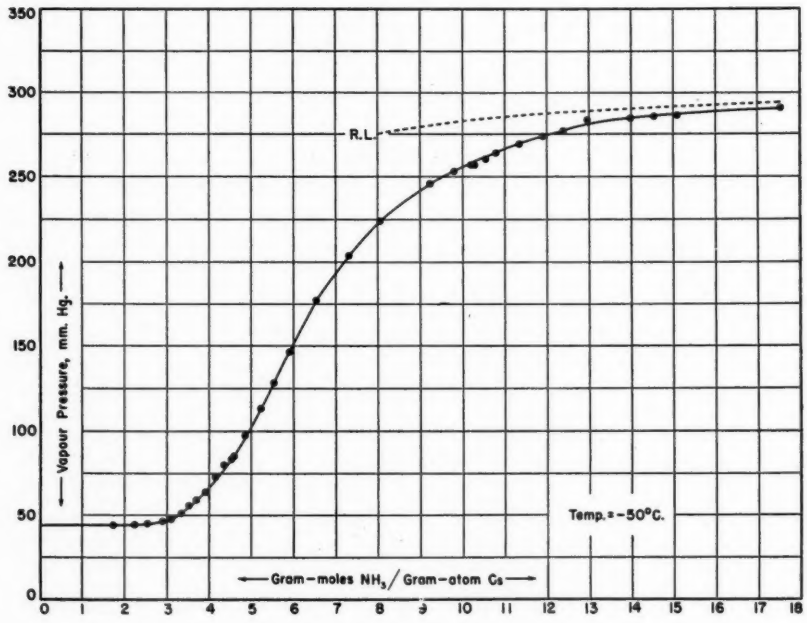

FIG. 4. *Vapor pressure – concentration curve for cesium–ammonia solutions.*

Fig. 4 represents a vapor pressure of 291.8 mm. for a solution of concentration about 2 *N*—a vapor pressure depression of 18.9 mm. For the same concentration of a solution that obeys Raoult's law, the vapor pressure depression

would be 16.75 mm. Accordingly, as one would expect, the deviation from Raoult's law is considerable for a 2 *N* solution; the concentration at which the solution first shows departure from Raoult's law was not determined in this experiment, since its accuracy would be low compared with that of a tensimeter measurement. For stronger solutions the atomic weight of cesium calculated on the basis of Raoult's law is markedly less than 132.91 (e.g., for point 21 on the curve the gram-atomic weight is 54.6). These observations are in agreement with those made by many workers on the vapor pressures of sodium solutions in ammonia. The increase in vapor pressure in passing from a saturated solution to those slightly less concentrated in metal is quite gradual, in contrast to that shown by the curve for sodium–ammonia solutions, in which the change is very abrupt. This probably indicates that ammonia is considerably more soluble in cesium than in sodium. The concentration of a saturated solution of cesium in ammonia at −50° C., as obtained from the vapor pressure curve, is 77.05% by weight (NH_3 : Cs ratio = 2.34).

2. Density of Cesium–ammonia Solutions

The results of these experiments are expressed in the graph comprising Fig. 5, and in Table II.

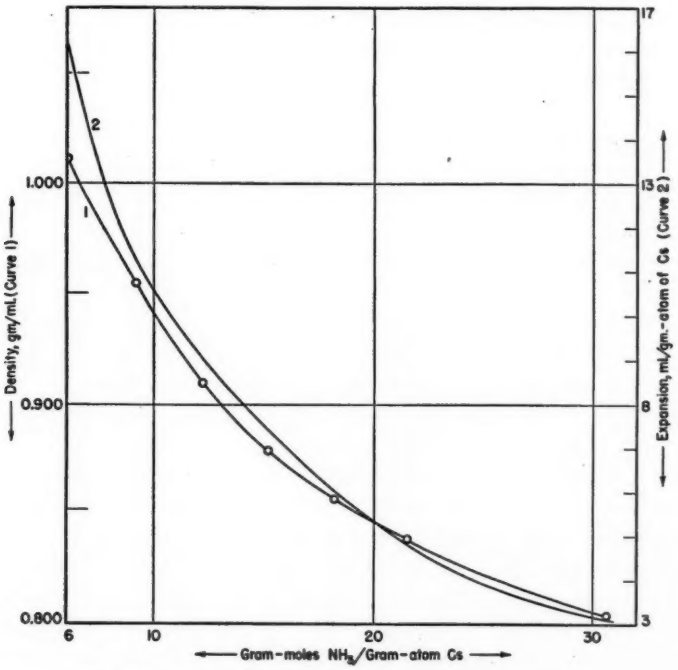

FIG. 5. *Density of cesium–ammonia solutions at −50° C.*

TABLE II

Solution No.	Mole ratio NH_3 : Cs	Density, gm. per ml.	Expansion, ml. per gm-atom of Cs
1	6.12	1.0140	16.2
2	9.20	0.9545	11.0
3	12.20	0.9095	9.2
4	15.25	0.8788	7.5
5	18.19	0.8570	6.1
6	21.55	0.8392	4.7
7	30.60	0.8041	3.1

For the calculation of the expansion of the solution per gram atom of cesium, the following data were used:

Wt. of cesium used in this experiment = 2.1725 gm.
Density of metallic cesium at −50° C. = 1.927 (8, p. 35).
Density of ammonia at −50° C. = 0.7020 (4).

The maximum expansion measured was somewhat less than that recorded for sodium in ammonia (14), and the variation with concentration is much more pronounced.

3. Electrical Conductance Measurements

The values for the conductance of cesium solutions in liquid ammonia at −70° C. are given in Table III.

TABLE III

Soln. No.	Mole ratio NH_3 : Cs	$N'y$	log V	K	λ
6	7.88	4.00	−0.718	650.0	162,500
7	11.40	2.99	−0.558	400.0	133,000
8	14.93	2.40	−0.440	222.0	92,600
9	18.49	2.00	−0.348	89.6	44,800
10	21.98	1.72	−0.273	23.8	13,830
11	25.50	1.51	−0.208	3.12	2070
12	28.96	1.35	−0.150	1.36	993
13	32.50	1.21	−0.102	0.81	670
14	36.0	1.10	−0.059	0.63	572
16	55.2	0.74	0.127	0.332	449
17	111.1	0.38	0.434	0.133	354
18	159.5	0.26	0.589	0.084	318
21	980.0	0.04	1.377	0.016	381

In the above table, V, the dilution, is the number of liters of solvent containing 1 gm-atom of solute, K is the specific conductance, and λ is the equivalent conductance. The conductance of the concentrated solutions, as one would expect, varies enormously with concentration. At a concentration of about 0.2 N, the equivalent conductance passes through a minimum of about 300 reciprocal ohms. The most concentrated solution measured, 4 N,

has a specific conductance of 650 reciprocal ohms, or about 1/16 that of metallic mercury. If comparison is made of these results with those for sodium–ammonia solutions, some care must be exercised because of an error in calculation made by C. A. Kraus (13, p. 761), which has been quoted in subsequent

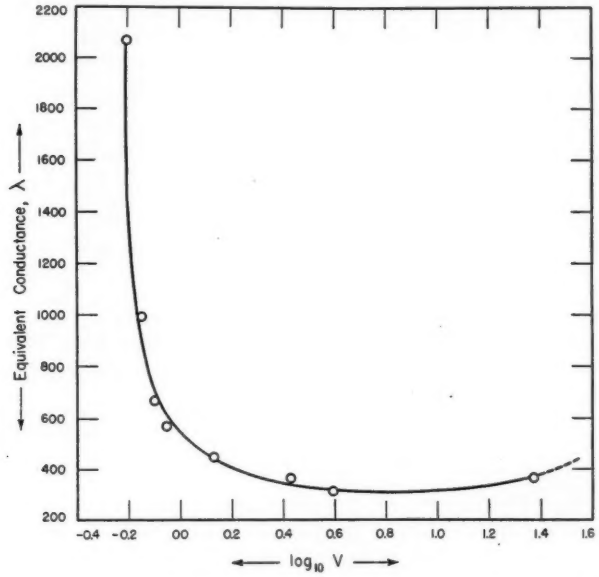

FIG. 6. *Electrical conductance of cesium–ammonia solutions at −70° C.*

literature (11). The statement cited from his paper that the specific conductance of a 2 *N* solution of sodium in ammonia is 1/6 that of metallic mercury is in error, since the conductance figures show that the factor should be 1/60.

The values of the conductance of cesium–ammonia solutions at − 70° C. have the order of magnitude that one would predict for them on the basis of the temperature coefficients derived by Kraus (13) for sodium solutions.

No evidence was found in all the work done with the cesium–ammonia solutions of any formation of two liquid phases down to −70° C. The conductances were investigated over a concentration range of 0.04 to 7 *N* and in no instance was there any change in the conductance at −70° C. on agitation of the solution in the cell. It has therefore been concluded that the cesium–ammonia solutions do not undergo the liquid–liquid phase separation in the concentration and temperature regions noted.

Since no region of liquid phase separation has been established, an arbitrarily chosen solution of 0.49 *M* ($NH_3 : Cs = 82.5$) was investigated for superconducting properties at liquid nitrogen temperatures. The apparatus used

was that described in a previous publication (10). No positive results were obtained with 20 trials on this solution. Since Ogg's theory (20) has as a prerequisite, the formation of two liquid phases, these measurements were not extended.

The resistance of the cesium solutions, like that of the sodium solutions, plunges downward as the solutions are cooled in liquid air. A sample of 0.302 *M* was slowly frozen at − 78° C. The resistance rose in three minutes (starting at − 70° C.) from 140 ohms to 369 ohms, and then fell by the end of 10 min. to a value of 3 ohms. In liquid air, the resistance was 0.4 ohm. This behavior is similar to that observed by Birch and MacDonald for sodium solutions (1), and is also doubtless due to the formation of a eutectic, since the solid at liquid air temperature is silver colored, like the sodium solutions, and unlike the frozen lithium solution, which is bronze in color.

Discussion

1. The vapor pressure curve indicates that the departure from Raoult's law is similar to that shown by sodium solutions. The solubility at −50° C. is 77.05% by weight.

2. The solutions show an expansion at −50° C. of 16.2 ml. per gm-atom of cesium for a NH_3 : Cs concentration of 6.1, falling off to a value of 3.1 for NH_3 : Cs of 30.6.

3. The conductance of the cesium solutions at −70° C. goes through a minimum at a concentration of 0.2 *N*. In magnitude, the conductance of the concentrated solutions approaches that of metals.

4. There is no separation into two liquid phases down to −70° C. for solutions between 0.04 *N* and 7 *N*.

As mentioned in the introduction, this investigation was carried out as a sequel to an earlier one in which some indication of persistent currents was observed in certain solutions of sodium in ammonia when frozen in liquid air. Since there was no similar phenomenon in the cesium solutions used, the work has now been discontinued. It now appears unlikely that the persistence of these currents in the sodium solutions is attributable to the superconducting state; a short discussion of this point is now under preparation.

Acknowledgment

The author is glad of this opportunity to acknowledge his indebtedness to Dr. E. A. Flood of the National Research Council for his advice and assistance in this investigation. Most of the above work was performed in Dr. Flood's laboratory and this is an opportune time to express thanks to the Chemistry Division of the National Research Council of Canada for this and for many other courtesies extended during the past several years.

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SOME NOTES ON THE PROPERTIES OF METAL–AMMONIA SOLUTIONS[1]

By J. W. Hodgins and E. A. Flood

Abstract

Some experiments are described that corroborate earlier observations of minute persistent currents in frozen rings of solutions of sodium in ammonia. It is shown, however, that it is unlikely that these currents are due either to superconductivity of the solid or to orientation of crystals in the magnetic field. Comment is made on the presence of two liquid phases in lithium–ammonia solutions.

I. Persistent Current Measurements

In 1946, the author published (6) what was to be the only corroboration of some observations by R. A. Ogg, Jr. (8) of the persistence of currents induced in certain frozen solutions of sodium in liquid ammonia. Numerous other investigators have reported negative results for the same experiments (2, 3, 5); Gibney and Pearson (4), on the basis of the low values that they obtained for the magnetic susceptibility, discredit the postulate that the frozen solid is superconducting.

In the face of such adverse opinion, it was thought advisable to repeat the experiments for the detection of persistent currents induced in frozen rings of solution. The same apparatus was used as was described in (6), but some changes were made in the technique. Liquid nitrogen was used as the refrigerant to avoid the possible interference from paramagnetic oxygen. Also the sequence of operation was as follows:

1. The ring of liquid solution at $-40°$ C. (mole ratio $NH_3 : Na = 25 : 1$) was suspended in the center of a solenoid producing a magnetic flux of 1600 gauss.
2. The ring of solution was carefully frozen by immersion in liquid nitrogen.
3. After two minutes, the nitrogen was removed and a search coil immediately placed under the frozen ring (the search coil was out of circuit at this stage).
4. The magnetic field was shut off, causing the flux to decay through the horizontal ring, and the search coil was connected to a galvanometer about 1/10 second later.
5. Any deflection of the galvanometer must be due to a change in the magnetic field about the search coil caused by a persistent current in the ring of solution.

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6. Unless a galvanometer deflection was obtained, the solution was remelted in liquid ammonia after each observation and the procedure repeated. When a deflection was noted, however, the frozen ring was not allowed to melt but after the indications of current had disappeared the procedure was repeated with the magnetic flux in the reversed direction. Thus, if the ring were superconducting, the second deflection should be in the reverse direction.
7. Finally, the experiments were carried out in the magnetically quiet period of the day (1 to 6.30 a.m. in Ottawa) on a table on which all the apparatus was earthed to dissipate electrostatic charges. The sensitivity of the apparatus was such that 1 mm. galvanometer deflection corresponds to 8 ma. in a single turn of conductor. This denotes a change in field of 2×10^{-3} gauss.

Out of 40 trials made, only 5 galvanometer deflections were observed. The largest of these corresponded to 32 ma. of current in the ring of solution and lasted for less than 20 sec. However, the direction of this "persistent current" did not change with the direction of the magnetic field as it should if the ring were superconducting. And yet no rapid galvanometer deflections of this magnitude had been observed when the magnetic field in the room was monitored over long periods with the search coil.

If the currents observed were due not to the superconducting property of the frozen solution, but were caused by the occasional preferred orientation of charge by the action of the magnetic field on crystals in the frozen solution, then the fact that the solution was in the form of a ring would be of no importance. To check this point the experiments were repeated on a solution (mole ratio $NH_3 : Na = 25 : 1$) in the form of a bar with an electrode at each end. The solution was frozen in the magnetic field as before and the field discontinued after two minutes' refrigeration in liquid nitrogen. About 1/10 sec. later a galvanometer was connected between the electrodes. Forty such experiments yielded negative results.

Accordingly, the following conclusions must be drawn:

(*a*) It is unlikely that solutions of sodium in ammonia (concentration about 1 *N*) are superconductors when frozen in liquid nitrogen.

(*b*) The sporadic currents observed are not due to magnetically oriented charged crystals in the frozen solution.

All the other "ring" experiments reported (including those of Ogg himself) were carried out with the solution in contact with the atmosphere. This introduces so many additional variables that it is no longer proper to refer to the system as sodium–ammonia, since there will be contamination by oxide, hydroxide, and ice, not to mention the uncertainty of composition. Accordingly it is felt that while other investigators reached the same conclusions as above, the inferences drawn were not completely justified by their means of attainment.

II. Liquid–liquid Phase Separation in Lithium and Cesium Solutions in Ammonia

Birch and MacDonald (1, p. 737) state, "It can be concluded that liquid–liquid phase separation above −78° C. is exhibited by all except lithium, although a slight doubt exists in the case of potassium."

In the preceding publication the author found no evidence of liquid–liquid phase separation with cesium solutions down to −70° C. in the concentration range from 0.050 *N* to 7 *N*. Also, there is no doubt that lithium solutions do separate into two liquid phases above −78° C. This was pointed out first by Kraus and Johnson (7), who observed a flat portion in the vapor pressure curve at −39.4° C. between the concentration $NH_3 : Li = 25$ and $NH_3 : Li = 45$ (mole ratios).

To check this point a solution of mole ratio $NH_3 : Li = 15.5 : 1$ was made up in a conductance cell with tiny platinum electrodes at the bottom of a trough running across the cell. The resistance of the solution was measured at a series of temperatures between −38° C. and −70° C. The solution was allowed to stand 10 min. at each temperature before the resistance was determined. A sharp increase in resistance occurred at about −60° C.; this indicated the formation of a second liquid phase. And indeed, at −70° C. the two phases were clearly visible, the characteristic bronze layer surmounting the deep blue solution.

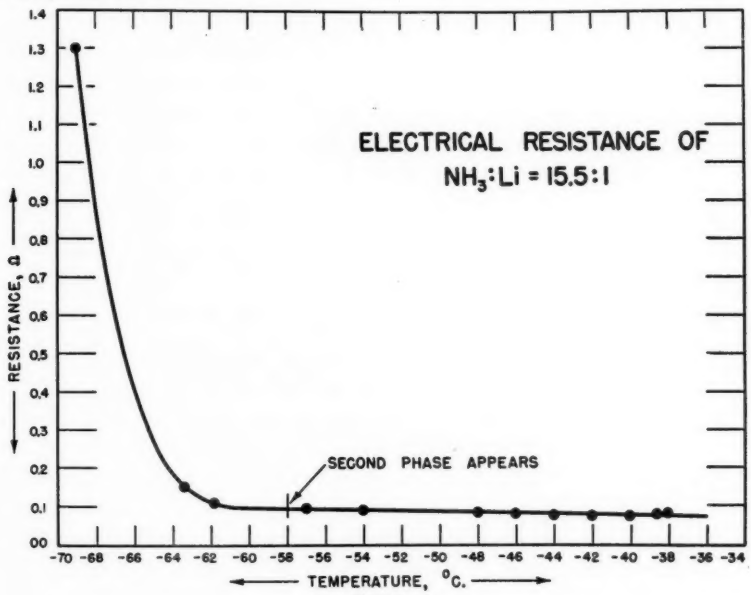

FIG. 1

Thus the statement of Birch and MacDonald should be amended to read, "Liquid–liquid phase separation above −78° C. is exhibited by all except *cesium*. . . ."

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